

UNCLASSIFIED
AD 410207

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

SOLID-STATE AND MOLECULAR THEORY GROUP, M.I.T. Q.P.R. No. 49, July 15, 1963

410207

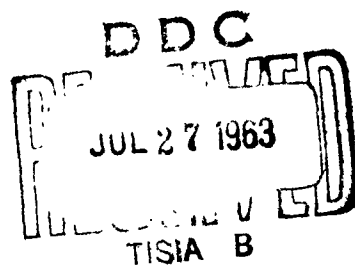
AD NO. 410207

DDC FILE COPY

QUARTERLY PROGRESS REPORT
NUMBER 49 JULY 15, 1963

SOLID-STATE AND
MOLECULAR THEORY GROUP

MASSACHUSETTS INSTITUTE
OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS



The research reported in this document was made possible through support extended the Massachusetts Institute of Technology, Department of Physics, by the Navy Department (Office of Naval Research), under O. N. R. Contract Nonr-1841(34); by the Army, Navy, and Air Force (Lincoln Laboratory), under Purchase Order P. O. C-00663; by the National Science Foundation, under Grant NSF-G10821; by the Air Force and the Advanced Research Projects Agency (Air Force Cambridge Research Laboratory), under Contract AF 19(628)-356. Reproduction in whole or in part is permitted for any purpose by the United States Government.

25.0 30

(7-1) 110

12NA

2-10-63

(2) 93p.

(13) 111

(14) 114

(12) 117

(17) 111

(17) 111

(19) 114

(20) 2L

(3) 111

(9) QUARTERLY PROGRESS REPORT
NUMBER 49 JULY 15, 1963

(6) SOLID-STATE AND
MOLECULAR THEORY GROUP

MASSACHUSETTS INSTITUTE
OF TECHNOLOGY

O. N. R. Contract Nonr-1841(34)

N. S. E. Grant NSF-G24908

A. F. C. R. L. Contract AF 19(628)-356

PERSONNEL

i.

Faculty

Professor J. C. Slater, Director

Professor M. P. Barnett

Professor G. F. Koster

Professor J. H. Wood

Staff Members, Research Assistants, Graduate Students

M. J. Bailey

I. G. Csizmedia

J. P. Dahl

P. DeCicco

D. E. Ellis

R. Englman

L. Gunther

M. C. Harrison

L. F. Mattheiss

J. Moskowitz

C. Nielson

R. M. Pitzer

P. M. Scop

C. M. Sonnenschein

B. T. Sutcliffe

A. C. Switendick

L. Szasz

J. P. Wright

Visiting Fellow

A. J. Freeman*

Secretary

Margaret Viles

* Staff member, National Magnet Laboratory, MIT.

Survey	1
1. Basis Functions for the Double Point Groups J. C. Slater	4
2. Energy Bands in Nickel Oxide A. C. Switendick	41
3. SCF Calculations on Neon, Using Gaussian Functions M. C. Harrison	70
4. SCF Calculations of Hydrogen Fluoride, Using Gaussian Functions M. C. Harrison	74
5. Gaussian Orbital Exponents M. C. Harrison and I. G. Csizmadia	78
6. Magnetic Dipole-Dipole Integrals Over Gaussian Functions M. C. Harrison	82
7. Molecular Integrals Over Slater Orbitals D. E. Ellis	85
8. The Pi Electronic Structure of the Benzene Molecule J. W. Moskowitz and M. P. Barnett	86

Quarterly Progress Report No. 49
of
Solid-State and Molecular Theory Group, M. I. T.
including work sponsored by
O. N. R. Contract Nonr-1841(34)
N. S. F. Grant NSF-G24908
A. F. C. R. L. Contract AF 19(628)-356

SURVEY

As I mentioned in the Survey of the April 15, 1963 Quarterly Progress Report, I have written a report on the double point groups, to supplement the material which has been presented in several recent Progress Reports on various space groups. This contribution is neither very original nor very complete. However, I felt that the material on the double groups in the literature was somewhat difficult for a beginner to read, and it seemed worth while to present a treatment, along the lines which I had been using for the single groups, which would introduce the reader to the general ideas, as well as to a number of specific applications. It is becoming very clear that for energy band studies of crystals containing atoms of even moderately high atomic number, the treatment of the spin-orbit and other relativistic effects is imperative, and the use of the double groups is just as necessary here as the use of the single groups is for any energy band problem. I hope that this contribution will help in making the technique of treating these problems more widely understood.

Dr. Switendick gives in the present Quarterly Progress Report an account more complete than he has given previously of his work on the energy bands in NiO. This account covers most of the work in his thesis. Since his conclusions are interesting, and since the behavior of NiO has caused a great deal of speculation in the past, it may be worth while for me to summarize the situation here. NiO has the sodium chloride structure. It is known to be an insulator, and to be antiferromagnetic. If it were built out of ions, the Ni^{++} ion would have eight electrons outside the argon shell, and the O^{--} ion would have a completed neon shell. One would conclude that the Ni^{++} ion, with only eight out of the ten d electrons present, would have a partially filled d band, which would lead to conducting properties, contrary to what is found. Switendick's first calculation, a straightforward one, verifies this fact.

With a magnetic material, however, there can be two separate energy bands, one for spins up, the other for spins down. These bands would be separated by an exchange effect. It could be that one of these bands would be depressed enough so that it would be filled, the other raised enough so that it would be partly empty. Each of these bands would hold five electrons per atom, so that if the lower one were full, and the upper one contained three electrons per atom, we should account for the proper number of electrons. The second part of Switendick's calculation is an estimate of the amount of separation between these two bands, and the verification that the upper band falls in the general region of the band containing the outer oxygen electrons, so that this upper d band might reasonably be partly filled.

Even this, however, would not lead to the insulating properties of nickel, unless the upper d band were split, by a crystalline field effect, into a lower occupied band holding three electrons, and an upper empty one holding two. This is the sort of crystal field effect which is often seen, and it is not unreasonable. The third part of Switendick's work is a demonstration that the integrals resulting in the crystal splitting might plausibly be great enough, in this case, to produce such a splitting.

This work of Switendick is very preliminary, with many unfinished points, but nevertheless it points a way to what might be an explanation of this puzzling substance, an explanation which had been suspected years ago, but which was too vague to believe without quantitative calculation. Before it can be accepted, one must make the calculation self-consistent, to get a reasonable estimate of the amount of charge in each of the ions, and to give a reliable estimate of the splitting of the bands, which depends greatly on the ionicity. Also one must set up the calculation in a form appropriate to an anti-ferromagnetic substance; Switendick's calculation is more suited to a hypothetical ferromagnetic case. Furthermore, one must examine the experimental fact that the crystal remains insulating above the Neel temperature, and its implications regarding the band structure. In spite of these shortcomings, still the present work represents real progress. It should be pointed out that though real self-consistency is not achieved, nevertheless Switendick has taken one step in this direction: he has investigated the charge distribution arising from his wave functions, the first step toward computing the field of this charge distribution, and hence toward an iterative approach to self-consistency.

This question of self-consistency, using the APW method, is one with which I have been concerned recently. In the Quarterly Progress Report of next October, I hope to report investigations into approximate ways of determining the potential throughout the crystal arising from the actual charge distribution found by the APW method, and the correction of the method to take account of this potential, rather than being limited to the present case of

spherical potentials within the spherical atoms, and a constant potential between. The first step involved in this is a careful study of the Ewald problem of finding the potential arising from a lattice of positive point charges, plus a uniformly distributed negative charge density. This study, in which I have had the assistance of Mr. de Cicco, is now completed, and as I mentioned, will be reported in the next Progress Report.

In addition to this work on crystalline problems and energy bands, the group working on molecular structure and integrals has been very active. Dr. Harrison reports his work on the use of Gaussian wave functions, which of course is originally an outgrowth of the work of Boys, and which a number of members of the group are concerned with. We are actively working on these methods along with the zeta-function method of Barnett and Coulson, and cross-checks are proving very valuable. Harrison has been testing his results on neon and HF, and has been developing rules for the optimum choice of parameters for the Gaussians. At the same time Ellis and others are going on with work on the zeta-function method, and are making good progress, so that applications to various molecules can be expected soon. The work which Moskowitz has been doing in collaboration with Barnett on benzene is reported in the present contribution in more detail than previously.

Since the preceding Quarterly Progress Report Drs. Quelle and Woznick have left the group, as mentioned in the preceding Quarterly Progress Report. Dr. Mattheiss left on June 1, 1963, to take a position with the Bell Telephone Laboratories, Inc., at Murray Hill, where he will continue his energy band work. We have had an added member of the group working on molecular structure, Russell M. Pitzer, who has been informally connected with the group for some months. He was working for his doctorate in the chemistry department at Harvard, and joined the group after completion of the requirements for the degree, taking an active part in the molecular calculations. He will be leaving during the summer to take a position at the California Institute of Technology. Several other members will also be leaving shortly, as will be mentioned in the next Quarterly Progress Report. We also have a new graduate student, Leon Gunther, who has just started work.

J. C. Slater

BASIS FUNCTIONS FOR THE DOUBLE POINT GROUPS

John C. Slater

I. Introduction

The point groups operate on functions of the coordinates, and consist of rotations and reflections which leave one point in space invariant. They are fundamental to the study of the space groups. As is well known, the continuous group of all rotations has one irreducible representation for each odd dimensionality $2l+1$, where l is an integer going from zero to infinity. The basis functions can be taken to be the $2l+1$ spherical harmonics corresponding to the values of m from $-l$ to l . In atomic problems with integral quantum numbers, we can associate the various irreducible representations with different values of the quantum number equal to the total angular momentum of the system.

This formulation of the problem has no place for the half-integral quantum numbers. In quantum mechanics we are familiar with half-integral angular momenta l , such that m , going from $-l$ to l by integral steps, has an even rather than an odd number of values, so that we meet irreducible representations of even dimensionality. We cannot use ordinary functions of space as basis functions for such irreducible representations. We must rather use spin-orbitals, composed of a function of space, and a spin function, which can be taken to be formed from the two Pauli spin functions α and β . In elementary treatments of quantum mechanics, one is used to having the spin quantized only along a fixed axis, usually the z axis, or the axis of spherical polar coordinates or cylindrical coordinates. Then we have the functions α and β , the first representing the case where the spin is along the $+$ direction along the axis, the second representing the case where the spin is along the $-$ direction. Once we start rotating axes in space, however, we meet a more general situation in which we must describe the possibility that the spin points along any arbitrary direction.

There is an immediate complication which arises, as soon as we consider the rotation of axes as applied to the functions α and β . Let us first consider only rotation about the z axis, so that the axis of quantization remains fixed. In many ways the functions α and β resemble ordinary spherical harmonics set up, in some sort of way, for half-integral l 's, in particular for $l = 1/2$. This would lead to $m = 1/2, -1/2$, so that since the dependence of a spherical harmonic on ϕ , the angle of rotation around the axis of the polar coordinates, is $e^{im\phi}$, we may suppose that α acts like the function $e^{i\phi/2}$, and β like $e^{-i\phi/2}$. The complication then arises if we make a rotation through an angle 2π . If ϕ increases by 2π , the function $e^{i\phi/2}$ is multiplied by $e^{\pi i} = -1$, so that α (and similarly β) changes sign on a rotation through 2π . We must rotate through 4π to come back to the original value of the function. This complication is the origin of the idea of the double group. For every rotation lying within a range 2π (for example, for every rotation in the range from 0 to 2π , or from $-\pi$ to π), we must have another rotation greater or less than this by 2π , whose effect on any function of coordinates will be identical to that of the original rotation, but whose effect on a spin function will give the negative of the value given by the original rotation.

In particular, suppose we are considering a point group of the ordinary type, consisting of a finite set of rotations, or rotations plus inversions, leaving a point invariant, and transforming a Hamiltonian function into itself. If we let the operations of this group operate on a function of spin, corresponding to a half-integral angular momentum, we shall find as in the preceding paragraph that for each operation involving a rotation, there will be another one corresponding to a rotation greater by 2π , which will give a function of opposite sign when applied to a basis function involving a spin. We shall have, then, twice as many operations to consider as in the ordinary group, which is the reason for describing it as a double group.

We must proceed over again from the beginning in discussing this double group. We must find its multiplication table, prove that it in fact is a group, investigate its classes, and find its irreducible representations and basis functions for them. These quantities do not follow trivially from those of the single group. We can see, however, that each of the basis functions and irreducible representations found for the single group, and involving integral quantum numbers, and functions of the coordinates only, will also supply basis functions and irreducible representations for the double groups. The reason is trivial: the new operations of the double group have the same effect on a function of coordinates alone that the original operations had. Aside from these irreducible representations, however, there will be other irreducible representations, called the extra representations, whose basis functions must be written in a form involving the spin functions. These extra representations have been discussed by various writers, in particular by Koster¹. However, these discussions are very

brief, and our object in the present note is to amplify the discussion, and to indicate specifically how basis functions can be set up. This is preliminary to a treatment of the double groups for the space groups found in crystal theory. There, when we consider spin-orbit interaction, we are treating the motion of an electron with a spin in a periodic potential, and we are interested in the type of wave functions which we shall find. These must be basis functions for one of the extra irreducible representations of the double group.

2. The Effect of a Rotation on the Spin Functions

We shall start our discussion by considering the effect of a rotation of axes on the Pauli functions α and β . We can derive the results by analogy from the case of the single groups. It has been shown by Wigner² that if we rotate axes according to the Euler angles a, b, c (which we shall define in a moment), a spherical harmonic $Y_{lm}(\theta, \phi)$ will be transformed into a linear combination of spherical harmonics $Y_{lm'}(\theta, \phi)$ with all values of m from $-l$ to l . This is the explicit statement of the fact mentioned in the preceding section, that this set of spherical harmonics forms a set of basis functions for an irreducible representation of the rotation group. The transformation can be written in the form given below:

$$Y_{lm}(\theta', \phi') = \sum (m') D^{(l)}_{mm'}(R)^* Y_{lm'}(\theta, \phi) \quad (1)$$

where the coefficients of the transformation are given by

$$D^{(l)}_{mm'}(abc) = \sum(t) \frac{(-1)^t \sqrt{(l+m)! (l-m)! (l+m')! (l-m')!}}{(l-m-t)! (l+m'-t)! t! (t+m-m')!} \\ \times e^{i(ma+m'c)} \left(\cos \frac{b}{2}\right)^{2l+m'-m-2t} \left(\sin \frac{b}{2}\right)^{2t+m-m'} \quad (2)$$

In Eq. (1) the rotation is characterized by the symbol R , which is equivalent to the three Euler angles a, b, c of Eq. (2). The index t is to run over those values for which all the factorials are those of positive integers or zero. The Euler angles are indicated in Fig. 1. The rotation of axes is defined as follows. One first rotates the coordinates about the z axis, in a positive direction, so as to carry x toward y , through an angle c , leading to axes $x', y', z' = z$. Next one rotates about the new y' axis, called the line of nodes, through an angle b , leading to axes $x'', y'' = y', z''$. Finally one rotates about the new z'' axis through an angle a . The final rotated axes $x'''y'''z'''$ lead to a final set of spherical polar coordinates $r\theta'\phi'$, such that θ' is the colatitude measured from

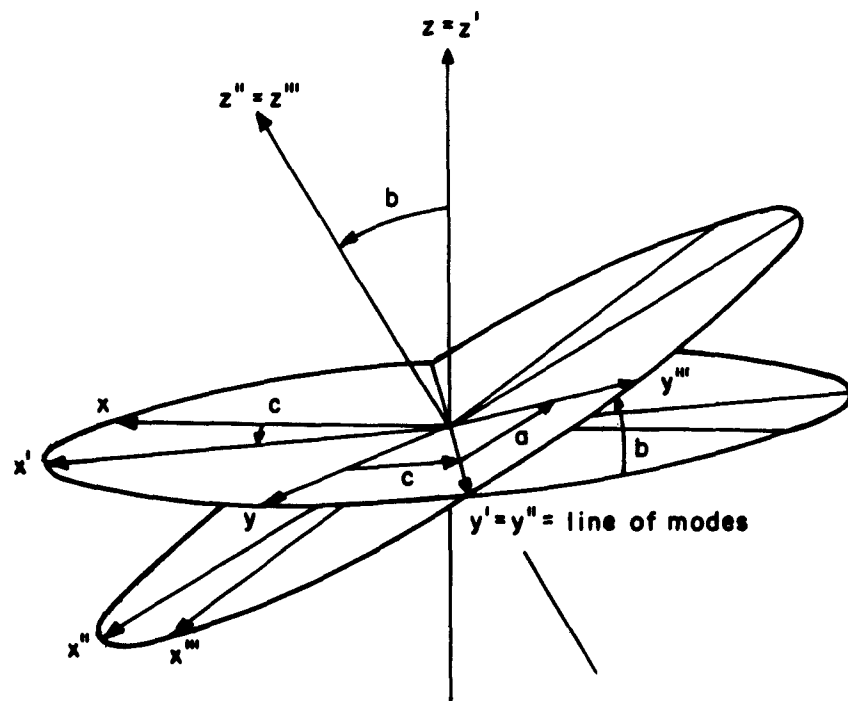


Fig. 1. Euler's angles for rotation of spherical harmonics.

the z''' axis and ϕ' is the angle of rotation from the x''' axis in the $x'''y'''$ plane, rotating in a positive direction about the z''' axis.

We shall shortly convert this statement of Euler's angles into rectangular coordinates, making it easier to understand. Before doing so, however, let us proceed with Eq. (2). If the spin can really be considered like an angular momentum vector of quantum number $1/2$, we should be able to find the transformation functions for the spin by specializing Eqs. (1) and (2) for the case $l = 1/2$, $m = \pm 1/2$. We find from Eq. (2) that

$$\begin{aligned} D^{(1/2)}_{(abc)1/2, 1/2} &= \cos \frac{b}{2} e^{i(a+c)/2} \\ D^{(1/2)}_{(abc)1/2, -1/2} &= \sin \frac{b}{2} e^{i(a-c)/2} \\ D^{(1/2)}_{(abc)-1/2, 1/2} &= -\sin \frac{b}{2} e^{i(-a+c)/2} \\ D^{(1/2)}_{(abc)-1/2, -1/2} &= \cos \frac{b}{2} e^{i(-a-c)/2} \end{aligned} \quad (3)$$

If we symbolize the rotation operator as R , we expect that the value of $R\alpha$ will be the corresponding function of (θ', ϕ') , just as with a function of coordinates we should have

$$Rf(\theta, \phi) = f(\theta', \phi') \quad (4)$$

Hence, from Eq. (1), we expect that we shall have

$$\begin{aligned} R\alpha &= D^{(1/2)}_{(abc)1/2, 1/2}^* \alpha + D^{(1/2)}_{(abc)1/2, -1/2}^* \beta \\ R\beta &= D^{(1/2)}_{(abc)-1/2, 1/2}^* \alpha + D^{(1/2)}_{(abc)-1/2, -1/2}^* \beta \end{aligned} \quad (5)$$

from which we have

$$\begin{aligned} R\alpha &= \cos \frac{b}{2} e^{-i(a+c)/2} \alpha + \sin \frac{b}{2} e^{-i(a-c)/2} \beta \\ R\beta &= -\sin \frac{b}{2} e^{-i(-a+c)/2} \alpha + \cos \frac{b}{2} e^{-i(-a-c)/2} \beta \end{aligned} \quad (6)$$

These are the standard equations for the effect of a rotation on the Pauli spin functions.

While we have merely derived these equations by analogy with the ordinary equations for the transformation of a spherical harmonic under a rotation of coordinates, there is sound reason for using the same method for the spin functions. We recall that there is a close relation between the rotation and the angular momentum operators³, so that the rotation operators can be written explicitly in terms of angular momentum operators. Furthermore, we know that the angular momentum operators for the electron spin satisfy the same basic equations (commutation rules, etc.) as ordinary angular momentum operators, so that the matrix elements of spin angular momentum follow the same formulas as those for ordinary orbital angular momentum. Hence one could carry through a rigorous proof that the effect of a rotation on the spin functions would have to be given by Eq. (6), as given above.

We have mentioned that it is more convenient to describe our rotations in terms of rectangular coordinates than in terms of Euler's angles. Therefore let us investigate the form which Eq. (6) takes when we describe our rotation in the form

$$Rf(x, y, z) = f(a_{11}x + a_{12}y + a_{13}z, a_{21}x + a_{22}y + a_{23}z, a_{31}x + a_{32}y + a_{33}z) \quad (7)$$

in which the a 's represent an orthogonal transformation with determinant of unity. For this purpose we shall throw the transformation of coordinates described by Euler's angles into the form given by Eq. (7). First we are directed to rotate about the z axis in the positive direction, through an angle c . This transforms the coordinates x, y, z into

$$\begin{aligned} x' &= x \cos c + y \sin c \\ y' &= -x \sin c + y \cos c \\ z' &= z \end{aligned} \quad (8)$$

Next we rotate about the y' axis through an angle b . This transforms x', y', z' into

$$\begin{aligned} x'' &= x' \cos b - z' \sin b \\ y'' &= y' \\ z'' &= x' \sin b + z' \cos b \end{aligned} \quad (9)$$

Finally we rotate about z'' through an angle a :

$$\begin{aligned} x''' &= x'' \cos a + y'' \sin a \\ y''' &= -x'' \sin a + y'' \cos a \\ z''' &= z'' \end{aligned} \quad (10)$$

We now combine these equations, so as to write x''' , y''' , z''' in terms of x , y , z . We find $x''' = a_{11}x + a_{12}y + a_{13}z$, etc., where

$$\begin{aligned}
 a_{11} &= \cos a \cos b \cos c - \sin a \sin c \\
 a_{12} &= \cos a \cos b \sin c + \sin a \cos c \\
 a_{13} &= -\cos a \sin b \\
 a_{21} &= -\sin a \cos b \cos c - \cos a \sin c \\
 a_{22} &= -\sin a \cos b \sin c + \cos a \cos c \\
 a_{23} &= \sin a \sin b \\
 a_{31} &= \sin b \cos c \\
 a_{32} &= \sin b \sin c \\
 a_{33} &= \cos b.
 \end{aligned} \tag{11}$$

If we are given the rotation in rectangular coordinates, in terms of a_{ij} , we can use Eq. (11) to solve for a , b , c , which can then be substituted into Eq. (6) to find the transformation of the spin functions. If $a_{33}^2 \neq 1$, we can solve Eq. (11) to give

$$\begin{aligned}
 \sin a &= \pm \frac{a_{23}}{\sqrt{1-a_{33}^2}} & \cos a &= \mp \frac{a_{13}}{\sqrt{1-a_{33}^2}} \\
 \sin b &= \pm \sqrt{1-a_{33}^2} & \cos b &= a_{33} \\
 \sin c &= \pm \frac{a_{32}}{\sqrt{1-a_{33}^2}} & \cos c &= \mp \frac{a_{31}}{\sqrt{1-a_{33}^2}}
 \end{aligned} \tag{12}$$

The upper signs are all to be used together, or the lower signs. If $a_{33}^2 = 1$, so that the denominators in Eq. (12) become zero, we must proceed differently. We have two cases, $a_{33} = \pm 1$. We have the following situation:

Case 1, $a_{33} = 1$

$$a_{11} = a_{22} = \cos(a+c), \quad a_{12} = -a_{21} = \sin(a+c)$$

Case 2, $a_{33} = -1$

$$a_{11} = -a_{22} = -\cos(a-c), \quad a_{12} = a_{21} = \sin(a-c) \tag{13}$$

In these latter cases, only $a+c$ or $a-c$ can be determined, but examination of Eq. (6) shows that in these cases it is only these combinations which will appear in the transformation.

We can now find the transformations from the a_{ij} 's, but when we carry the process through, we find that there is an ambiguity in the result. From Eqs. (12) or (13) we find the angles a, b, c , up to an additive constant of 2π . However, in Eq. (6), it is half of these angles which appear. Hence if any of the angles is increased by 2π , the coefficients of Eq. (6) change sign. This is the ambiguity which we have referred to in the first section: corresponding to each operator of the point group we find two operators of the double group. We shall denote one of these operators as R , the other as \bar{R} ; we take up later the question as to which of the two to denote as R , which as \bar{R} . We find on examination that the ambiguity of sign resulting from the \pm in Eq. (12) does not introduce any additional ambiguity into the final results; we can just as well use only the upper sign in Eq. (12), and we shall get the same final answers.

3. Examples of Rotation of Coordinates

Now we shall carry through some specific examples to illustrate the application of these methods. Let us first carry out a rotation about the z axis, which therefore does not change the axis of quantization. This is such a rotation as we meet in the operations of the group C_N , where the operator X_q is defined by the equation⁴

$$X_q \psi(\phi) = \psi(\phi + \frac{2\pi q}{N}) \quad (14)$$

If we put this into rectangular coordinates, we have $x = r \cos \phi$, $y = r \sin \phi$, $z = z$ (where r, ϕ, z are cylindrical coordinates). Thus $\psi(\phi + \frac{2\pi q}{N})$ stands for

$$\psi(r \cos(\phi + \frac{2\pi q}{N}), r \sin(\phi + \frac{2\pi q}{N}), z) \quad (15)$$

When we work this out, it becomes

$$\psi(x \cos \frac{2\pi q}{N} - y \sin \frac{2\pi q}{N}, x \sin \frac{2\pi q}{N} + y \cos \frac{2\pi q}{N}, z) \quad (16)$$

so that we have

$$\begin{aligned} a_{11} &= \cos \frac{2\pi q}{N}, & a_{12} &= -\sin \frac{2\pi q}{N}, & a_{13} &= 0 \\ a_{21} &= \sin \frac{2\pi q}{N}, & a_{22} &= \cos \frac{2\pi q}{N}, & a_{23} &= 0 \\ a_{31} &= 0, & a_{32} &= 0, & a_{33} &= 1 \end{aligned} \quad (17)$$

We then have Case 1 of Eq. (13), leading to

$$\cos(a+c) = \cos \frac{2\pi q}{N}, \quad \sin(a+c) = -\sin \frac{2\pi q}{N} \quad (18)$$

from which the obvious solution is $a+c = -2\pi q/N$, though we could also have a value 2π greater. Since $a_{33} = \cos b = 1$, we have $b = 0$ (or 2π). If we choose $b = 0$, $a+c = -2\pi q/N$, and substitute into Eq. (6), we have

$$X_q \alpha = e^{\pi i q/N} \alpha, \quad X_q \beta = e^{-\pi i q/N} \beta \quad (19)$$

These are just what we should expect from a quantum number of $1/2$ for α , $-1/2$ for β ; the general rule for the effect of X_q operating on a wave function like $e^{im\phi}$ is that $X_q e^{im\phi} = e^{2\pi i m q/N} e^{im\phi}$. We also have, however, the other case which arises when either the angle b , or $a+c$, is increased by 2π , in which case

$$\bar{X}_q \alpha = -e^{\pi i q/N} \alpha, \quad \bar{X}_q \beta = -e^{-\pi i q/N} \beta \quad (20)$$

It is obvious in this case that it is natural to define the unbarred and barred operators as we have done it in Eqs. (19) and (20), since the unbarred operators then agree with the ordinary rotation operators of the single group.

In the single group C_N , the multiplication table is very simple. If the operator X_q merely multiplies a basis function $e^{im\phi}$ by the factor $e^{2\pi i m q/N}$, and another operator X_p multiplies it by the factor $e^{2\pi i m p/N}$, it is obvious that the two operators operating in succession multiply it by $e^{2\pi i m (p+q)/N}$, so that $X_q X_p = X_p X_q = X_{p+q}$. In applying this rule, we must be careful of the fact that we have operators for only a restricted range of subscripts, which may be taken to be $-\frac{N}{2} < q \leq \frac{N}{2}$. If the sum $p+q$ lies outside this range, we are to bring it back into the range by adding or subtracting integral multiples of N . But now we see that we have a difficulty with the double group. Changing q by N , according to Eqs. (19) and (20), will introduce an extra factor $e^{\pi i N/N} = e^{\pi i} = -1$ into the resulting function. In other words, if we add or subtract N to bring an operator back into the allowed range, we must change from an unbarred to a barred operator, or vice versa. We have, in fact,

$$X_{q \pm N} = \bar{X}_q \quad (21)$$

This will, then, modify the multiplication table of a double group, introducing bars in some cases of product operations, not in others. By using this rule, we find that the multiplication table for the double group C_3 , as a simple example, is as given in Table 1.

Table 1

Multiplication Table for the Double Group C_3 . The table gives the product of the operator along the left (first factor) and that at the top (second factor).

	X_0	X_1	X_{-1}	\bar{X}_0	\bar{X}_1	\bar{X}_{-1}
X_0	X_0	X_1	X_{-1}	\bar{X}_0	\bar{X}_1	\bar{X}_{-1}
X_1	X_1	\bar{X}_{-1}	X_0	\bar{X}_1	X_{-1}	X_0
X_{-1}	X_{-1}	X_0	\bar{X}_1	\bar{X}_{-1}	X_0	X_1
\bar{X}_0	\bar{X}_0	\bar{X}_1	\bar{X}_{-1}	X_0	X_1	X_{-1}
\bar{X}_1	\bar{X}_1	X_{-1}	X_0	X_1	\bar{X}_{-1}	X_0
\bar{X}_{-1}	\bar{X}_{-1}	X_0	X_1	X_{-1}	X_0	\bar{X}_1

We note that among the products arising from two unbarred operators there are two barred operators, namely $X_1 X_1 = \bar{X}_{-1}$, $X_{-1} X_{-1} = \bar{X}_1$. Thus we cannot use the multiplication table for the single group without change for the double group. We note one simplifying feature, however: the product of an unbarred and a barred operator is the same as the product of the two corresponding unbarred operators, except with a change from unbarred to barred, or vice versa. In other words, changing from barred to unbarred operators is like a change of sign. This means that the multiplication table for unbarred operators, which is only a fourth as large as the complete multiplication table, really furnishes complete information. In other words, it is no more complicated to write down the multiplication table for a double group than for the corresponding single group. We shall henceforth take advantage of this fact in writing multiplication tables.

The double group C_3 is isomorphic with the single group C_6 ; according to Eq. (21), we could label the barred operators \bar{X}_0 , \bar{X}_1 , \bar{X}_{-1} by the symbols X_3 , X_{-2} , X_2 respectively, and we should then have the operators X_0 , $X_{\pm 1}$, $X_{\pm 2}$, X_3 of the single group C_6 . The multiplication table of Table 1 follows at once from that for the single group C_6 . As in that case, the group is Abelian, each operator forms a class by itself, and there are six one-dimensional irreducible representations. Since the single group C_3 has three one-dimensional irreducible representations, this means that there are also three extra

one-dimensional irreducible representations for the double group. In general, we see that the double group C_N is isomorphic with the single group C_{2N} .

Next let us take up quite a different sort of rotation, one in which the axis of quantization changes. Thus, let us take a cyclic permutation of axes, in which z shifts to x , x shifts to y , y to z , so that

$$Rf(x, y, z) = f(y, z, x) \quad (22)$$

As we compare with Eq. (7), we see that this is the case

$$\begin{aligned} a_{11} = a_{13} = a_{21} = a_{22} = a_{32} = a_{33} &= 0, \\ a_{12} = a_{23} = a_{31} &= 1 \end{aligned} \quad (23)$$

We may now use Eq. (12) to derive the Euler angles, and if we choose the upper signs, we have

$$\begin{aligned} \sin a &= 1, \cos a = 0 \\ \sin b &= 1, \cos b = 0 \\ \sin c &= 0, \cos c = 1 \end{aligned} \quad (24)$$

The solutions may be taken to be $a = \pi/2$, $b = \pi/2$, $c = 0$. Then in Eq. (6) we have

$$\begin{aligned} R\alpha &= \cos \frac{\pi}{4} e^{-\pi i/4} \alpha + \sin \frac{\pi}{4} e^{-\pi i/4} \beta \\ &= \frac{1-i}{2} (\alpha + \beta) \\ R\beta &= -\sin \frac{\pi}{4} e^{\pi i/4} \alpha + \cos \frac{\pi}{4} e^{\pi i/4} \beta \\ &= \frac{1+i}{2} (-\alpha + \beta) \end{aligned} \quad (25)$$

Since we have rotated the z axis into the x direction, we should suppose that the resulting spin functions denoted as $R\alpha$ and $R\beta$ respectively in Eq. (25) would represent spins pointing along the $\pm x$ directions. We shall shortly show that this is the case.

Similarly let us rotate so that z goes into y , y into x , x into z . Here as in Eq. (23) we have all the a 's equal to zero except now a_{13} , a_{21} , a_{32} , which are unity. From Eq. (12) we have in this case

$$\begin{aligned} \sin a &= 0, \cos a = -1 \\ \sin b &= 1, \cos b = 0 \\ \sin c &= 1, \cos c = 0 \end{aligned} \quad (26)$$

from which $a = -\pi$, $b = c = \pi/2$. Then from Eq. (6) we find

$$Ra = \frac{1+i}{2} a + \frac{-1+i}{2} \beta = \frac{1+i}{2} (a + i\beta)$$

$$R\beta = \frac{1+i}{2} a + \frac{1-i}{2} \beta = \frac{1+i}{2} (a - i\beta) \quad (27)$$

These functions should represent spin functions along y and $-y$ respectively. In choosing the value of a , from Eq. (26), we might well have hesitated as to whether to choose $-\pi$, as we did, or π ; one would have given R , the other \bar{R} . We have made the choice in such a way that this operator, and the preceding one worked out in Eq. (25), which belong to the same class in the point group O_h , will have the same character of unity. We shall see later that this forms one guide as to the choice of the primed and unprimed operations.

4. Relation of Double Groups to Dirac's Electron Theory

The fundamental theory of the electron spin is of course Dirac's theory, and the results we have been discussing must arise from that theory. By stating the relation of our methods to those of Dirac, we can clarify the situation. We shall follow closely the discussion of Dirac's methods given by the present author⁵. It is well known that Dirac uses a wave function with four components, $\psi_1, \psi_2, \psi_3, \psi_4$. If we are dealing with an electron, ψ_1 and ψ_2 are small, ψ_3 and ψ_4 large. The function ψ_3 represents in a way the wave function for electrons of $+$ spin, or associated with the spin function α , while the function ψ_4 is the wave function for electrons of $-$ spin. Thus in a way we can write the complete wave function, in terms of spin-orbitals, in the form $\psi_3\alpha + \psi_4\beta$. From the results of Eqs. (25) and (27), we should expect that if $\psi_4 = 0$, the spin is along z ; if $\psi_3 = 0$, it is along $-z$; if $\psi_3 = \psi_4$, it is along x ; if $\psi_3 = -\psi_4$, along $-x$; if $\psi_4 = i\psi_3$, along y ; and if $\psi_4 = -i\psi_3$, along $-y$. We shall shortly show in an independent way that this is true.

If ψ_3 and ψ_4 are proportional to the same functions of x, y, z , then their ratio will remain fixed over all space, and this means that the spin orientation will be the same everywhere. If on the other hand we wish to represent a situation in which the spin orientation varies from point to point, ψ_3 and ψ_4 must be different functions of x, y , and z . Such a situation arises in case we are dealing with spin waves in which the spin orientation varies in a helical manner as we pass through a crystal. We shall not have to deal with that situation in the present note.

In Ref. 5, Section 23-6, it is shown that the x, y , and z components of spin at a given point of space are proportional to

$$\begin{aligned}
s_x &= \psi_3^* \psi_4 + \psi_4^* \psi_3 \\
s_y &= -i\psi_3^* \psi_4 + i\psi_4^* \psi_3 \\
s_z &= \psi_3^* \psi_3 - \psi_4^* \psi_4
\end{aligned} \tag{28}$$

If ψ_3 and ψ_4 are normalized so that $\psi_3^* \psi_3 + \psi_4^* \psi_4 = 1$, the quantities of Eq. (28) are the components of unit vector in the direction of the spin. Thus if $\psi_3 = 1$, $\psi_4 = 0$, corresponding to a zero coefficient for the Pauli function β , we see from Eq. (28) that $s_z = 1$, $s_x = s_y = 0$. Similarly if $\psi_3 = 0$, $\psi_4 = 1$, $s_z = -1$. If $\psi_3 = \psi_4 = 1/\sqrt{2}$, $s_x = 1$, $s_y = s_z = 0$, while if $\psi_3 = -\psi_4 = 1/\sqrt{2}$, $s_x = -1$. Again, if $\psi_4 = i\psi_3$, $s_y = -1$. These are the cases considered in Eqs. (25) and (27). The fact that the wave functions in those cases differ from those considered here by being multiplied by a complex constant of magnitude unity makes no difference in Eq. (28).

In other words, we can check the rotated wave functions of Eqs. (25) and (27) and show that the spins in fact point in the directions we expect. It is easy by using the same methods to set up a linear combination of α and β representing a spin pointing in any arbitrary direction. Thus, let s_x , s_y , s_z , which are three components of a unit vector, have arbitrary values. Since $\psi_3^* \psi_3 + \psi_4^* \psi_4 = 1$, we see from Eq. (28) that

$$\begin{aligned}
s_z &= \psi_3^* \psi_3 - (1 - \psi_3^* \psi_3) = 2\psi_3^* \psi_3 - 1, \\
\psi_3^* \psi_3 &= (1 + s_z)/2
\end{aligned} \tag{29}$$

Now let $\psi_4/\psi_3 = a+bi$, where a and b are real. Then from Eq. (28) we have

$$s_x = \psi_3^* \psi_3 (a+bi+a-bi) = 2a\psi_3^* \psi_3 = a(1+s_z),$$

so that

$$a = \frac{s_x}{1+s_z} \tag{30}$$

Similarly we have

$$\begin{aligned}
s_y &= \psi_3^* \psi_3 (-ia+b+ia+b) = 2b\psi_3^* \psi_3, \\
b &= \frac{s_y}{1+s_z}
\end{aligned} \tag{31}$$

We thus know the absolute magnitude of ψ_3 , and the ratio ψ_4/ψ_3 . This is as much as we can find from s_x, s_y, s_z . If in particular we choose ψ_3 to be real, we have

$$\psi_3 = \sqrt{\frac{1+s_z}{2}}, \quad \psi_4 = \frac{s_x + is_y}{\sqrt{2(1+s_z)}} \quad (32)$$

These formulas will be useful in our future work, to allow us to set up wave functions corresponding to spins pointing in arbitrary directions.

So far we have been considering the rotations and their effect on the spin functions α and β . We also have operations including reflections, or inversions. It is most convenient to write each such operation as the product of an inversion and a rotation. Since we have found how to handle a rotation, we need only investigate in addition the effect of an inversion on the spin functions. The answer is very simple: an inversion leaves the functions invariant. The reason for this can be seen easily from the discussion we have just been giving. Suppose we are dealing with a central-field problem, as a simple example. Then both of the functions ψ_3 and ψ_4 will be either even or odd on inversion. The inversion operation then will not change the expressions of Eq. (28), and hence will not affect the spin. This is not a proof, but it suggests the correctness of the result, which can be proved rigorously in general. Hence we can show that the effect of any operation involving both an inversion and a rotation on the spin functions α and β is identical with that of the rotation alone. This gives us all the information we need to discuss the double groups completely.

5. The Double Groups C_{Nv}

We are now ready to proceed with some actual cases, and shall first consider the general double group C_{Nv} , and in particular the examples of C_{2v} , C_{3v} , and C_{4v} . The single group has not only the operations X_q , defined in Eq. (14), which are met in the group C_N , but also the operations Y_q , defined by

$$Y_q \psi(\phi) = \psi(-\phi + \frac{2\pi q}{N}) \quad (33)$$

or in rectangular coordinates

$$Y_q \psi(x, y, z) = \psi(x \cos \frac{2\pi q}{N} + y \sin \frac{2\pi q}{N}, x \sin \frac{2\pi q}{N} - y \cos \frac{2\pi q}{N}, z) \quad (34)$$

This is an improper rotation, consisting of a rotation and an inversion. If we denote the corresponding rotation alone as Y'_q , we have

$$Y'_q \psi(x, y, z) = \psi(-x \cos \frac{2\pi q}{N} - y \sin \frac{2\pi q}{N}, -x \sin \frac{2\pi q}{N} + y \cos \frac{2\pi q}{N}, -z) \quad (35)$$

which corresponds to

$$\begin{aligned} a_{11} &= -\cos \frac{2\pi q}{N}, \quad a_{12} = -\sin \frac{2\pi q}{N}, \quad a_{13} = 0 \\ a_{21} &= a_{12}, \quad a_{22} = -a_{11}, \quad a_{23} = 0 \\ a_{31} &= a_{32} = 0, \quad a_{33} = -1 \end{aligned} \quad (36)$$

We have an example of Case 2 of Eq. (13), leading to $b = \pi$, $\cos \frac{2\pi q}{N} = \cos(a-c)$, $\sin \frac{2\pi q}{N} = -\sin(a-c)$, so that $a-c = -2\pi q/N$. Then from Eq. (6) we have

$$Y'_q \alpha = e^{\pi i q/N} \beta, \quad Y'_q \beta = -e^{-\pi i q/N} \alpha \quad (37)$$

In Eq. (37), coupled with Eq. (19), we have the statement of the effect of the operations of the group on the functions α and β . We have a relation

$$Y_q^{\pm N} = Y_q \quad (38)$$

analogous to Eq. (21).

We shall now use Eqs. (19), (21), (37), and (38) to give the effect of the operators X_q and Y_q on α and β , for the groups C_{2v} , C_{3v} , and C_{4v} ; we remember that since the inversion does not affect the spin functions, the effect of Y_q is the same as that of Y'_q . We shall present these results in the form of matrix elements:

$$R\alpha = R_{11}\alpha + R_{21}\beta, \quad R\beta = R_{12}\alpha + R_{22}\beta \quad (39)$$

where R is one of the operators, and R_{11} , etc., are the matrix elements of the operator. We give the results for the three groups in question in Table 2.

We notice that each of the operators of the group, acting on the two basis functions α and β , produces a linear combination of these two functions. Thus they form basis functions for an irreducible representation of the group. Each double group has such a two-dimensional irreducible representation, for which the two spin functions are basis functions, just as each single group has a totally symmetrical one-dimensional irreducible representation in which the basis function is unchanged under each of the operations of the group. We note that in Table 2 we have given the matrix elements only for the unbarred operators of the double groups; the matrix elements for a barred operator are the negatives of those for the corresponding unbarred operator.

Table 2

Matrix elements of the two-dimensional irreducible representations of the double groups C_{2v} , C_{3v} , C_{4v} , using α and β as basis functions. The matrix elements for the barred operators are the negatives of those for the unbarred operators.

 C_{2v}

	X_0	X_1	Y_0	Y_1
11	1	i	0	0
21	0	0	1	i
12	0	0	-1	i
22	1	-i	0	0
χ	2	0	0	0

 C_{3v}

	X_0	X_1	X_{-1}	Y_0	Y_1	Y_{-1}
11	1	$e^{\pi i/3}$	$e^{-\pi i/3}$	0	0	0
21	0	0	0	1	$e^{\pi i/3}$	$e^{-\pi i/3}$
12	0	0	0	-1	$-e^{\pi i/3}$	$-e^{-\pi i/3}$
22	1	$e^{-\pi i/3}$	$e^{\pi i/3}$	0	0	0
χ	2	1	1	0	0	0

 C_{4v}

	X_0	X_1	X_{-1}	X_2	Y_0	Y_1	Y_{-1}	Y_2
11	1	$e^{\pi i/4}$	$e^{-\pi i/4}$	i	0	0	0	0
21	0	0	0	0	1	$e^{\pi i/4}$	$e^{-\pi i/4}$	i
12	0	0	0	0	-1	$-e^{\pi i/4}$	$-e^{-\pi i/4}$	i
22	1	$e^{-\pi i/4}$	$e^{\pi i/4}$	-i	0	0	0	0
χ	2	$\sqrt{2}$	$\sqrt{2}$	0	0	0	0	0

It is convenient next to set up multiplication tables for the groups. This is done in Table 3.

Table 3

Multiplication tables for the double groups C_{2v} , C_{3v} , and C_{4v} . The tables give the product of the operator along the left (first factor) and that at the top (second factor). For the product of one unbarred and one barred operator, barred and unbarred operators are to be interchanged in the products. The products of two barred operators are identical with those of two unbarred operators.

 C_{2v}

	X_0	X_1	Y_0	Y_1
X_0	X_0	X_1	Y_0	Y_1
X_1	X_1	\bar{X}_0	\bar{Y}_1	Y_0
Y_0	Y_0	Y_1	\bar{X}_0	\bar{X}_1
Y_1	Y_1	\bar{Y}_0	X_1	\bar{X}_0

 C_{3v}

	X_0	X_1	X_{-1}	Y_0	Y_1	Y_{-1}
X_0	X_0	X_1	X_{-1}	Y_0	Y_1	Y_{-1}
X_1	X_1	\bar{X}_{-1}	X_0	Y_{-1}	Y_0	\bar{Y}_1
X_{-1}	X_{-1}	X_0	\bar{X}_1	Y_1	\bar{Y}_{-1}	Y_0
Y_0	Y_0	Y_1	Y_{-1}	\bar{X}_0	\bar{X}_1	\bar{X}_{-1}
Y_1	Y_1	\bar{Y}_{-1}	Y_0	\bar{X}_{-1}	\bar{X}_0	X_1
Y_{-1}	Y_{-1}	Y_0	\bar{Y}_1	\bar{X}_1	X_{-1}	\bar{X}_0

Table 3 (continued)

C_{4v}	X_0	X_1	X_{-1}	X_2	Y_0	Y_1	Y_{-1}	Y_2
X_0	X_0	X_1	X_{-1}	X_2	Y_0	Y_1	Y_{-1}	Y_2
X_1	X_1	X_2	X_0	\bar{X}_{-1}	Y_{-1}	Y_0	\bar{Y}_2	Y_1
X_{-1}	X_{-1}	X_0	\bar{X}_2	X_1	Y_1	Y_2	Y_0	\bar{Y}_{-1}
X_2	X_2	\bar{X}_{-1}	X_1	\bar{X}_0	\bar{Y}_2	Y_{-1}	\bar{Y}_1	Y_0
Y_0	Y_0	Y_1	Y_{-1}	Y_2	\bar{X}_0	\bar{X}_1	\bar{X}_{-1}	\bar{X}_2
Y_1	Y_1	Y_2	Y_0	\bar{Y}_{-1}	\bar{X}_{-1}	\bar{X}_0	X_2	\bar{X}_1
Y_{-1}	Y_{-1}	Y_0	\bar{Y}_2	Y_1	\bar{X}_1	\bar{X}_2	\bar{X}_0	X_{-1}
Y_2	Y_2	\bar{Y}_{-1}	Y_1	\bar{Y}_0	X_2	\bar{X}_{-1}	X_1	\bar{X}_0

It is simple to set up these tables, using the information which we already have. Thus, for example, let us consider the case of C_{2v} . From Table 2 we know that

$$X_1\alpha = i\alpha, Y_0\alpha = \beta, Y_1\alpha = i\beta, X_1\beta = -i\beta, Y_0\beta = -\alpha, Y_1\beta = i\alpha \quad (40)$$

Then for instance we have $X_1X_1\alpha = X_1(i\alpha) = -\alpha = \bar{X}_0\alpha$, as indicated in the table. We can verify this by computing the effect of X_1X_1 on β . We have $X_1X_1\beta = X_1(-i\beta) = -\beta = \bar{X}_0\beta$. Similar methods suffice to find each entry in the tables. As we have mentioned in the discussion of the group C_N in Section 3, it is only necessary to tabulate the products of unbarred operators in presenting the multiplication table, since putting a bar on an operator changes the product operator from barred to unbarred, or vice versa.

Once we have the multiplication table, we can find the classes of operations. We recall that if R_i^{-1} is the inverse operator to R_i , all operators $R_i^{-1}R_jR_i$ fall in the same class with R_j . By proceeding in this way, we find the following classes in the cases we are using as illustrations:

$$\begin{aligned}
C_{2v}: & \text{ five classes: } X_0; \bar{X}_0; X_1 \text{ and } \bar{X}_1; Y_0 \text{ and } \bar{Y}_0; Y_1 \text{ and } \bar{Y}_1 \\
C_{3v}: & \text{ six classes: } X_0; \bar{X}_0; X_1 \text{ and } X_{-1}; \bar{X}_1 \text{ and } \bar{X}_{-1}; Y_0, Y_1, \text{ and } \bar{Y}_{-1}; \\
& \bar{Y}_0, Y_{-1}, \text{ and } Y_{-1} \\
C_{4v}: & \text{ seven classes: } X_0; \bar{X}_0; X_1 \text{ and } X_{-1}; \bar{X}_1 \text{ and } \bar{X}_{-1}; X_2 \text{ and } \bar{X}_2; \\
& Y_0, Y_2, \bar{Y}_0, \text{ and } \bar{Y}_2; Y_1, Y_{-1}, \bar{Y}_1, \text{ and } \bar{Y}_{-1}. \quad (41)
\end{aligned}$$

In contrast to this, for the single groups we have the following classes:

$$\begin{aligned}
C_{2v}: & \text{ four classes: } X_0, X_1, Y_0, \text{ and } Y_1 \\
C_{3v}: & \text{ three classes: } X_0; X_1 \text{ and } X_{-1}; Y_0, Y_1, \text{ and } Y_{-1} \\
C_{4v}: & \text{ five classes: } X_0; X_1 \text{ and } X_{-1}; X_2; Y_0 \text{ and } Y_2; Y_1 \text{ and } Y_{-1} \quad (42)
\end{aligned}$$

We can now use this information to deduce the number of extra irreducible representations for each of the double groups. We recall that the number of irreducible representations for any group equals the number of classes, and the sum of the squares of the dimensionalities of the irreducible representations equals the number of operators in the group. Thus for the single group C_{2v} we have four one-dimensional irreducible representations; for the single group of C_{3v} we have two one-dimensional and one two-dimensional irreducible representation; for the single group of C_{4v} we have four one-dimensional and one two-dimensional irreducible representation. For the double group C_{2v} we have five irreducible representations, namely the four found for the single group, and an extra two-dimensional irreducible representation. For the double group C_{3v} we have six irreducible representations, namely the three found for the single group, and two extra one-dimensional and one extra two-dimensional irreducible representations. For the double group C_{4v} we have seven irreducible representations, namely the five found for the single group, and two extra two-dimensional irreducible representations. We shall now proceed to find basis functions and matrix elements for these extra representations.

We have pointed out that we already have basis functions for one extra two-dimensional irreducible representation in each case, namely the functions α and β , and we have tabulated the matrix elements in Table 2. For C_{2v} , this is the only extra irreducible representation. For C_{3v} , we must have two extra one-dimensional irreducible representation, and for C_{4v} an additional extra two-dimensional irreducible representation. We must now look at the problem more physically, to see how to set up basis functions for these extra representations, and hence to find the matrix elements.

The two functions α and β of course correspond to components $M_S = \pm 1/2$ of spin angular momentum along the axis. It seems rather obvious that if we are looking for further basis functions, we should build up functions corresponding to angular momentum $\pm 3/2$, or if necessary even greater half-integral values. Let us explore this possibility, using first the case C_{3v} as an example. We know that the functions of coordinates $e^{i\phi}$ and $e^{-i\phi}$ correspond to $M_L = \pm 1$ respectively. If we then set up functions $e^{i\phi}\alpha$ and $e^{-i\phi}\beta$, we should expect that they would correspond to total angular momentum along the axis, or M , of $\pm 3/2$ respectively. Let us then try these as basis functions. To find the effect of one of the operators on one of these functions, we must know its effect both on the function of coordinates, and on the function of spin. We have already investigated the effect on the spin. As for the coordinates, we have

$$\begin{aligned} X_q e^{\pm i\phi} &= e^{\pm 2\pi i q / N} e^{\pm i\phi} \\ Y_q e^{\pm i\phi} &= e^{\pm 2\pi i q / N} e^{\mp i\phi} \end{aligned} \quad (43)$$

Let us call our two functions $\psi_1 = e^{i\phi}\alpha$ and $\psi_2 = e^{-i\phi}\beta$ respectively, and let us examine the effect of the operators of the double group of C_{3v} on them. We have

$$\begin{aligned} X_1 \psi_1 &= e^{2\pi i / 3} e^{i\phi} e^{\pi i / 3} \alpha = -e^{i\phi} \alpha = -\psi_1 \\ X_1 \psi_2 &= -\psi_2, \quad X_{-1} \psi_1 = -\psi_1, \quad X_{-1} \psi_2 = -\psi_2 \\ Y_0 \psi_1 &= \psi_2, \quad Y_0 \psi_2 = -\psi_1, \quad Y_1 \psi_1 = -\psi_2, \quad Y_1 \psi_2 = \psi_1, \\ Y_{-1} \psi_1 &= -\psi_2, \quad Y_{-1} \psi_2 = \psi_1 \end{aligned} \quad (44)$$

The effects of the barred operators on the functions ψ_1 and ψ_2 are the negatives of those of the unbarred operators. We see, then, that ψ_1 and ψ_2 form basis functions for a two-dimensional representation of the double group C_{3v} . This is however a reducible representation. If we take new basis functions $\psi_1 \pm i\psi_2$, we find that each of these combinations forms a basis function for a one-dimensional irreducible representation. These then are the two extra one-dimensional irreducible representations which we are seeking, for C_{3v} . The matrix elements are given in Table 4.

Though we have found two one-dimensional irreducible representations, nevertheless we can prove that on account of time reversal they must be degenerate with each other, so that as far as energy is concerned, the

Table 4

Matrix elements and characters for the extra irreducible representations of the double group C_{3v} . The representations are labelled as for the group of the wave vector along the 111 axis, in the representations of the double space groups for a cubic crystal. Basis functions for Λ_4 and Λ_5 are $\psi_1 \pm i\psi_2$, where $\psi_1 = e^{i\phi}\alpha$, $\psi_2 = e^{-i\phi}\beta$, ϕ being the angle of rotation about the axis. Basis functions for Λ_6 are α , β , where in each case the spin is quantized along the axis. Note according to Section 6 of the text that for use with the cubic space groups, we must interchange the definitions of the operators Y_0 and \bar{Y}_0 so that the matrix elements of \bar{Y}_0 will take on the negatives of the values given in the table, which agrees with Eq. (37). Matrix elements for barred operators are the negatives of those tabulated.

	X_0	X_1	X_{-1}	Y_0	Y_1	Y_{-1}
Λ_4	1	-1	-1	-i	i	i
Λ_5	1	-1	-1	i	-i	-i
$(\Lambda_6)_{11}$	1	$e^{\pi i/3}$	$e^{-\pi i/3}$	0	0	0
$(\Lambda_6)_{21}$	0	0	0	1	$e^{\pi i/3}$	$e^{-\pi i/3}$
$(\Lambda_6)_{12}$	0	0	0	-1	$-e^{-\pi i/3}$	$-e^{\pi i/3}$
$(\Lambda_6)_{22}$	1	$e^{-\pi i/3}$	$e^{\pi i/3}$	0	0	0
$\chi(\Lambda_6)$	2	1	1	0	0	0

situation is no different from what it would have been with a two-dimensional representation. This is natural; we can see no reason why wave functions corresponding to $M = 3/2$ or $-3/2$ should have different energies, in the absence of an external field. Wigner⁶ has shown that there is a simple test as to whether additional degeneracy is introduced by time-reversal or not. One must construct the sum

$$\sum(R)\chi(R^2) \quad (45)$$

where we are summing over the operators R of a group, R^2 is the square of the operator in question, which can be found from the multiplication table, and we are to sum the characters of these squared operators, for the representation

in question. It can be shown that this sum must take one of three values; g , 0 , or $-g$, where g is the number of operators in the group. In either of the first two cases, where the sum is g or 0 , a new degeneracy will be introduced by spin reversal, if we are dealing with extra representations of the double group; in the third case it will not.

Let us apply this test in the present case. For C_{3v} we have twelve operators, X_0 , $X_{\pm 1}$, Y_0 , $Y_{\pm 1}$, and the corresponding barred operators. From the multiplication table, Table 3, we find that

$$X_0^2 = X_0, X_{\pm 1}^2 = \bar{X}_{\mp 1}, X_{-1}^2 = X_1, Y_0^2 = Y_1^2 = Y_{-1}^2 = \bar{X}_0 \quad (46)$$

The squares of the barred operators equal the squares of the corresponding unbarred operators. Now from Table 4 we know that for the first one-dimensional irreducible extra representations of C_{3v} the character of X_0 is 1 , and of $X_{\pm 1}$ it is -1 . We do not require the characters of the Y 's. The characters of the barred operators are the negatives of those of the unbarred operators. The sum of Eq. (45) is now

$$2[\chi(X_0) + \chi(\bar{X}_{-1}) + \chi(\bar{X}_1) + 3\chi(\bar{X}_0)] = 2(1 + 1 + 1 - 3) = 0 \quad (47)$$

Since this sum is zero, an extra degeneracy is introduced by time reversal, which in this case is the degeneracy between the two one-dimensional extra representations of C_{3v} . Just for reassurance, we may apply the same test to the two-dimensional irreducible representation of C_{3v} , which according to Table 2 has characters given by $\chi(X_0) = 2$, $\chi(X_1) = \chi(X_{-1}) = 1$, other characters being zero. Hence the sum in this case is $2(2 - 1 - 1 - 6) = -12$, or $-g$, so that no additional degeneracy is introduced by time reversal with this representation, which of course is correct.

Now let us take up the case of C_{4v} . We recall that there must be another two-dimensional irreducible representation, in addition to that given in Table 3. We naturally try the same two basis functions $\psi_1 = e^{i\phi\alpha}$ and $\psi_2 = e^{-i\phi\beta}$ here which we have used for C_{3v} . By methods similar to those already used, we find the matrix elements given in Table 5. This representation is irreducible, as it is expected to be.

6. Cubic Double Groups

We shall illustrate our methods further by taking two of the cubic double groups, namely T_d and O_h . These can conveniently be treated together, since the operations of O_h are merely those of T_d , and in addition those of T_d plus an inversion. Since the inversion has no effect on the spin functions, we can get complete information about the effect of the operations on the spin functions from the double group T_d . The single group has 24 operations,

Table 5

Matrix elements and characters for the extra irreducible representations of the double group C_{4v} . The representations are labelled as for the group of the wave vector along the 001 axis, in the representations of the double space groups for a cubic crystal. Basis functions for Δ_6 , α and β , and for Δ_7 , $e^{i\phi}\alpha$ and $e^{-i\phi}\beta$, where ϕ is the angle of rotation about the axis, and α and β are quantized with respect to this axis. Note as for C_{3v} , in Table 4, that for use with the cubic space groups we must change the signs of the matrix elements for Y_0 . Matrix elements for barred operators are the negatives of those tabulated.

	X_0	X_1	X_{-1}	X_2	Y_0	Y_1	Y_{-1}	Y_2
$(\Delta_6)_{11}$	1	$e^{\pi i/4}$	$e^{-\pi i/4}$	i	0	0	0	0
$(\Delta_6)_{21}$	0	0	0	0	1	$e^{\pi i/4}$	$e^{-\pi i/4}$	i
$(\Delta_6)_{12}$	0	0	0	0	-1	$-e^{\pi i/4}$	$-e^{-\pi i/4}$	i
$(\Delta_6)_{22}$	1	$e^{-\pi i/4}$	$e^{\pi i/4}$	-i	0	0	0	0
$\chi(\Delta_6)$	2	$\sqrt{2}$	$\sqrt{2}$	0	0	0	0	0
$(\Delta_7)_{11}$	1	$-e^{-\pi i/4}$	$-e^{\pi i/4}$	-i	0	0	0	0
$(\Delta_7)_{21}$	0	0	0	0	1	$-e^{-\pi i/4}$	$-e^{\pi i/4}$	-i
$(\Delta_7)_{12}$	0	0	0	0	-1	$e^{\pi i/4}$	$e^{-\pi i/4}$	-i
$(\Delta_7)_{22}$	1	$-e^{\pi i/4}$	$-e^{-\pi i/4}$	i	0	0	0	0
$\chi(\Delta_7)$	2	$-\sqrt{2}$	$-\sqrt{2}$	0	0	0	0	0

$R_1 \dots R_{24}$, defined on p. 9, QPR No. 47, January 15, 1963. The double group has of course 48 operations, the 24 of the single group plus the barred operations. Our first task is to find the effect of the 24 operations of the single group on the spin functions α and β .

To carry this out, we use the same methods which we have sketched previously. The operations $R_1 \dots R_{12}$ are rotations, while $R_{13} \dots R_{24}$ are rotations plus inversions, so that $R'_{13} \dots R'_{24}$, which consist of the original operations plus an inversion, are pure rotations, which together with $R_1 \dots R_{12}$ comprise the operations of the group O . For each of these it is easy to find the angles a, b, c , from Eqs. (11), (12), and (13), and hence to find the transformations of α and β by Eq. (6). For instance, we have $R_2 f(x, y, z) = f(x, -y, -z)$, so that $a_{11} = 1$, $a_{22} = a_{33} = -1$, all other a 's vanishing. This is an example of Case 2, Eq. (13), leading to $\cos(a-c) = -1$, $\sin(a-c) = 0$, from which $a-c = \pm\pi$, as well as $b = \pm\pi$. It proves more convenient, for reasons which we shall mention later, to take one of these signs to be $+$, the other $-$. In either such case we have

$$R_2 \alpha = i\beta, \quad R_2 \beta = i\alpha \quad (48)$$

Again, we have $R_5 f(x, y, z) = f(y, z, x)$, and $R_9 f(x, y, z) = f(z, x, y) = f(z, x, y)$. We have already discussed these two cases in Eqs. (25) and (27). As still another example, we have $R'_{13} f(x, y, z) = f(x, -z, y)$, from which $a_{11} = 1$, $a_{23} = -1$, $a_{32} = 1$. These lead according to Eq. (12) to $\sin a = -1$, $\cos a = 0$, $\sin b = 1$, $\cos b = 0$, $\sin c = 1$, $\cos c = 0$, from which we may assume $a = -\pi/2$, $b = c = \pi/2$. These lead to

$$\begin{aligned} R'_{13} \alpha &= \frac{1}{\sqrt{2}} (\alpha + i\beta) \\ R'_{13} \beta &= \frac{1}{\sqrt{2}} (i\alpha + \beta) \end{aligned} \quad (49)$$

These examples are enough to show how we derive the matrix elements for the operations acting on the basis functions α and β , which are tabulated in Table 6. This table is appropriate both for the double groups T_d and O_h . In the latter case we have the 24 operations $R_1 \dots R_{24}$, the primed operations $R'_1 \dots R'_{24}$ (each equal to the unprimed operation plus an inversion), and the 48 barred operations associated with these. Going from an unprimed to a primed operation makes no change in the matrix elements; going from an unbarred to a barred operation changes the sign of the matrix elements.

From this table of the effect of the operations on the basis functions α and β , we can proceed to find the multiplication table for the double groups T_d and O_h , using the same methods described in the preceding section. This multiplication table is given in Table 7. We give the table for the 24 operations $R_1 \dots R_{24}$. If one of the factors is primed, the product operation is primed; if both are primed, the product is unprimed. If one of the factors is barred, the product changes from unbarred to barred or vice versa. If both factors are barred, the product is as given in the table.

Table 6

Matrix elements for the two-dimensional irreducible representation of the double group T_d' with basis functions α and β . This is the representation denoted as Γ_6^+ or Γ_7^- in Eq. (53). The matrix elements of the barred operators are the negatives of those tabulated. For the double group O_h , the primed operations have the same matrix elements as the unprimed for Γ_6^+ , the negatives of these values for Γ_7^- , so that this table suffices for that case as well. The operations are defined on p. 9 of Quarterly Progress Report No. 47, or in Table A12-9, J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 1. Table lists in order the 11, 21, 12, and 22 matrix elements

R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}	R_{16}	R_{17}	R_{18}	R_{19}	R_{20}	R_{21}	R_{22}	R_{23}	R_{24}
1	0	0	i	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	0
0	i	-1	0	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	0	0	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{1+i}{\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$
0	1	1	0	$\frac{-1-i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{-1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	0	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{1+i}{\sqrt{2}}$	$-\frac{1+i}{\sqrt{2}}$	$\frac{-1-i}{\sqrt{2}}$
1	0	0	-i	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0
χ	2	0	0	1	1	1	1	1	1	1	1	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	0	0	0	0	0	0

Table 7

Multiplication table for the double group T_d . Table gives product operation R_k or \bar{R}_k of R_i (on left) and R_j (at top), $R_i R_j = R_k$. For the product of one unbarred and one barred operator, barred and unbarred operators are to be interchanged in the products. The products of two barred operators are identical with those of two unbarred operators.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
2	2	$\bar{1}$	$\bar{4}$	3	7	8	5	$\bar{6}$	$\bar{12}$	$\bar{11}$	10	9	$\bar{14}$	13	$\bar{21}$	$\bar{22}$	$\bar{24}$	23	20	$\bar{19}$	15	16	$\bar{18}$	17
3	3	4	$\bar{1}$	$\bar{2}$	8	7	6	5	$\bar{10}$	9	$\bar{12}$	11	$\bar{20}$	19	$\bar{16}$	15	$\bar{23}$	$\bar{24}$	$\bar{14}$	13	22	$\bar{21}$	17	18
4	4	$\bar{3}$	2	$\bar{1}$	6	5	$\bar{7}$	8	$\bar{11}$	12	9	$\bar{10}$	$\bar{19}$	$\bar{20}$	$\bar{22}$	21	$\bar{18}$	17	13	14	$\bar{16}$	15	24	$\bar{23}$
5	5	8	6	7	9	12	10	11	1	$\bar{4}$	$\bar{2}$	3	18	24	14	20	16	22	23	$\bar{17}$	$\bar{19}$	$\bar{13}$	$\bar{21}$	$\bar{15}$
6	6	7	5	$\bar{8}$	11	$\bar{10}$	12	9	4	1	3	$\bar{2}$	17	$\bar{23}$	$\bar{20}$	14	21	15	$\bar{24}$	18	$\bar{13}$	19	16	22
7	7	$\bar{6}$	8	5	12	9	$\bar{11}$	10	2	3	1	4	23	17	13	$\bar{19}$	$\bar{22}$	16	18	24	$\bar{20}$	14	$\bar{15}$	21
8	8	5	7	6	10	11	9	$\bar{12}$	3	2	$\bar{4}$	1	$\bar{24}$	18	19	13	15	$\bar{21}$	$\bar{17}$	23	14	20	$\bar{22}$	16
9	9	$\bar{11}$	$\bar{12}$	10	1	3	4	2	5	7	8	6	$\bar{22}$	15	$\bar{24}$	17	$\bar{20}$	13	$\bar{21}$	16	$\bar{23}$	18	$\bar{19}$	14
10	10	$\bar{12}$	11	9	3	1	2	$\bar{4}$	8	5	7	6	$\bar{21}$	16	18	23	13	20	22	$\bar{15}$	17	24	$\bar{14}$	$\bar{19}$
11	11	9	$\bar{10}$	12	$\bar{4}$	$\bar{2}$	1	3	6	8	7	5	15	22	$\bar{23}$	18	14	19	$\bar{16}$	$\bar{21}$	24	$\bar{17}$	13	20
12	12	10	9	$\bar{11}$	$\bar{2}$	4	3	1	7	5	6	8	16	21	17	24	$\bar{19}$	14	15	22	$\bar{18}$	$\bar{23}$	20	$\bar{15}$
13	13	$\bar{14}$	19	$\bar{20}$	16	15	$\bar{22}$	$\bar{21}$	$\bar{24}$	23	18	17	2	1	8	7	9	10	$\bar{4}$	3	6	5	$\bar{11}$	12
14	14	13	$\bar{20}$	$\bar{19}$	22	21	16	15	17	18	$\bar{23}$	24	1	$\bar{2}$	6	5	12	11	3	$\bar{4}$	8	7	10	9
15	15	$\bar{22}$	$\bar{16}$	21	18	$\bar{23}$	17	$\bar{24}$	$\bar{20}$	13	19	14	9	4	3	1	6	8	$\bar{12}$	10	$\bar{2}$	$\bar{4}$	7	5
16	16	$\bar{21}$	15	$\bar{22}$	24	17	23	18	13	20	14	$\bar{19}$	10	12	1	$\bar{3}$	7	5	11	9	4	$\bar{2}$	8	6
17	17	23	$\bar{24}$	$\bar{18}$	14	$\bar{20}$	$\bar{19}$	13	$\bar{22}$	16	15	21	7	6	9	12	4	1	8	5	$\bar{10}$	11	3	$\bar{2}$
18	18	$\bar{24}$	$\bar{23}$	17	20	14	13	19	15	$\bar{21}$	22	16	8	5	11	10	1	$\bar{4}$	7	6	12	9	2	3
19	19	$\bar{20}$	$\bar{13}$	14	$\bar{21}$	22	15	$\bar{16}$	$\bar{23}$	$\bar{24}$	$\bar{17}$	18	3	$\bar{4}$	7	8	11	$\bar{12}$	$\bar{1}$	2	5	6	9	10
20	20	19	14	13	$\bar{15}$	16	$\bar{21}$	22	18	$\bar{17}$	24	23	$\bar{4}$	3	5	6	10	9	2	$\bar{1}$	7	8	$\bar{12}$	$\bar{11}$
21	21	16	$\bar{22}$	$\bar{15}$	$\bar{23}$	$\bar{18}$	24	17	$\bar{19}$	14	$\bar{20}$	$\bar{13}$	12	$\bar{10}$	4	$\bar{2}$	8	6	9	11	$\bar{1}$	3	5	7
22	22	15	21	16	$\bar{17}$	24	18	$\bar{23}$	14	19	$\bar{13}$	20	11	9	$\bar{2}$	$\bar{4}$	5	7	$\bar{10}$	$\bar{12}$	3	$\bar{1}$	8	6
23	23	$\bar{17}$	18	$\bar{24}$	$\bar{19}$	13	$\bar{14}$	20	$\bar{21}$	$\bar{15}$	16	$\bar{22}$	5	7	10	$\bar{11}$	2	3	5	8	9	12	$\bar{1}$	4
24	24	18	17	23	$\bar{13}$	$\bar{19}$	20	14	16	22	21	$\bar{15}$	5	8	12	9	3	2	6	7	$\bar{11}$	$\bar{10}$	$\bar{4}$	$\bar{1}$

In setting up the matrix elements of Table 6, which result in the multiplication table of Table 7, we have a choice of sign with each operation; as mentioned earlier, we can call a given operation either R or \bar{R} . We have chosen the signs so as to get the closest connection possible with the results for C_{Nv} given previously. In the first place, we can carry out a cyclic permutation of variables, changing x into y , y into z , z into x . We must expect that we shall get the same form for the matrix elements under these circumstances, if at the same time we change the basis functions properly, going from α and β , which point along z , to the corresponding functions pointing along x , and then to those pointing along y . From Section 4 we know how to set up those basis functions. Our choices are made so that the matrix elements are unchanged by this type of transformation.

Next, we know that the group O_h has several subgroups of the form of C_{Nv} . We have tried as far as possible to arrange the definitions of the operations to agree with our earlier treatment of those groups. A complete agreement however is impossible, as we shall now show. First we have a two-fold rotation about the axis $x = y$, or alternatively about the z axis. In these two cases we have the following parallelism between operations of O_h , as we have described them, and the operations of the double group C_{2v} :

$$\text{Axis } x = y: R_1 \rightarrow X_0, R_{24}' \rightarrow X_1, R_4' \rightarrow Y_0, R_{23} \rightarrow Y_1$$

$$\text{z axis: } R_1 \rightarrow X_0, R_4 \rightarrow X_1, R_3' \rightarrow Y_0, R_2' \rightarrow Y_1 \quad (50)$$

We may then take out of Table 7 the part relating to these operations, rename the operators according to Eq. (50), and set up a multiplication table just for these operators. This table is given in Table 8; it is identical for either of the cases given in Eq. (50). We should expect it to be identical with the multiplication table for C_{2v} . When we compare with that multiplication table, in Table 3, we see that there are a number of cases where there is disagreement between barred and unbarred operators. This disagreement would all be removed if in Table 3 we had renamed the operator Y_0 , so that the operator which was called Y_0 in that table was called \bar{Y}_0 instead. Alternatively we could have renamed the corresponding operator R_4' or R_3' in Table 7, calling them \bar{R}_4' or \bar{R}_3' respectively. The latter procedure is impossible, however, for there is an inherent relation between the operations R_2, R_3, R_4 , demanded by the cyclic permutation symmetry of the problem, and if we were to change the definition of R_3' and R_4' we should have to change R_2' as well. Since they are all concerned in the second case of Eq. (50), we are not allowed to tamper with them. Hence the only way to keep consistency between the group O_h and C_{2v} is to change Y_0 in C_{2v} . As far as R_2, R_3, R_4 are concerned, they are fixed. This was the reason for choosing the definition of R_2 as was described in Eq. (48).

Table 8

Multiplication table for operators X_0, X_1, Y_0, Y_1 of double group C_{2v} , assuming identification of Eq. (50) with operators of group T_d , and using multiplication table of Table 7 for T_d .

	X_0	X_1	Y_0	Y_1
X_0	X_0	X_1	Y_0	Y_1
X_1	X_1	X_0	Y_1	Y_0
Y_0	Y_0	Y_1	X_0	X_1
Y_1	Y_1	Y_0	X_1	X_0

In a similar way we get parallelism between certain subgroups of O_h and C_{3v} and C_{4v} . Thus we have the relations given in Eq. (51):

For C_{3v}

$$R_1 \rightarrow X_0, R_9 \rightarrow X_1, R_5 \rightarrow X_{-1}$$

$$R_{23} \rightarrow Y_0, R_{21} \rightarrow Y_1, R_{19} \rightarrow Y_{-1}$$

For C_{4v}

$$R_1 \rightarrow X_0, R'_{17} \rightarrow X_1, R'_{18} \rightarrow X_{-1}, R_4 \rightarrow X_2$$

$$R'_3 \rightarrow Y_0, R_{23} \rightarrow Y_1, R_{24} \rightarrow Y_{-1}, R'_2 \rightarrow Y_2 \quad (51)$$

Here again we can set up multiplication tables for the groups C_{3v} and C_{4v} respectively out of the results of Table 7. Again there are certain discrepancies between Tables 7 and 3, and again they can be removed if we define Y_0 for the groups C_{3v} and C_{4v} oppositely to what we have done. That is, in place of $Y_0^\alpha = \beta, Y_0^\beta = -\alpha$, as given in Eq. (37), we must choose $Y_0^\alpha = -\beta, Y_0^\beta = \alpha$. On the other hand, we must continue to use Eq. (37) for all other values of q , aside from $q = 0$. The author is unable to say whether there is a deeper meaning in the fact that this change in the definition of Y_0 brings agreement between the various cases, or whether it is an accident. As we well know, there is no fundamental consideration determining whether a given operation is to be defined as barred or unbarred.

We have now determined the multiplication table for the groups T_d and O_h , and can next find the classes of operators in each case. We proceed as before, and find the following results:

Group T_d

Single group has five classes: $R_1; R_2, R_3, R_4; R_5 \dots R_{12}; R_{13} \dots R_{18}; R_{19} \dots R_{24}$. Consequently it has five irreducible representations, two one-dimensional, one two-dimensional, two three-dimensional.

Double group has eight classes: $R_1; \bar{R}_1; R_2, R_3, R_4, \bar{R}_2, \bar{R}_3, \bar{R}_4; R_5 \dots R_{12}; \bar{R}_5 \dots \bar{R}_{12}; R_{13} \dots R_{18}; \bar{R}_{13} \dots \bar{R}_{18}; R_{19} \dots R_{24}, \bar{R}_{19} \dots \bar{R}_{24}$. Consequently it has eight irreducible representations, consisting of those for the single group, two extra two-dimensional representations, and one four-dimensional.

Group O_h

Both for the single and double groups we have twice as many classes, and twice as many irreducible representations of each dimensionality, as for T_d . The additional representations found in O_h and not in T_d differ from those in that for each representation of T_d , we have two for O_h , one having the same matrix elements for each operator R' as for the corresponding operator R , the other having a matrix element for R' which is the negative of that for R .

Our problem is then to find basis functions, and matrix elements, for the two extra two-dimensional representations of T_d , and the extra four-dimensional representation. For O_h we need only produce the additional basis functions describing the property of being even or odd on inversion. We shall carry this out in the next section.

7. Basis Functions and Irreducible Representations for the Double Groups T_d and O_h

The first of the extra two-dimensional irreducible representations of T_d is already given in Table 6. It uses the basis functions α and β . We note that though we are dealing with cubic symmetry, we are using the z axis as a preferred axis, the axis of quantization of the functions α and β . We could, however, quantize along x or y equally well. If we use the basis functions of Eq. (25) we have quantization along x , and if we use those of Eq. (27) we have quantization along y . The matrix elements have the same form as in Table 6, except that the names of the operators are interchanged in a way which can be predicted from the cyclic permutation. In studying space groups and wave vectors in crystals, it is often convenient in such a case to take the axis of quantization along the reduced wave vector of the wave. Thus, if we are considering propagation along the x axis, rather than z , we may choose the basis functions of Eq. (25).

In addition to this two-dimensional irreducible representation, we must find another two-dimensional, and a four-dimensional irreducible representation. We can get at these representations by setting up basis functions according to a physical argument. The cubic symmetry comes by a perturbation of spherical symmetry. The two-dimensional representation using α and β as basis functions arises from an S function in a central field problem. When we combine a function of coordinates which is independent of angles, with the spin function, we are proceeding as if to build up the $^2S_{1/2}$ wave functions for $M = \pm 1/2$, in a central field problem. We naturally look for further basis functions by considering atomic functions of p symmetry, which will not be split in a cubic field. We know that an atomic p function, without spin, has three components, corresponding to $M_L = 1, 0, -1$. When we couple this with a spin, with $M_S = \pm 1/2$, we can get $M = 3/2$ and $1/2$ by coupling the spin to $M_L = 1$, $M = 1/2$ and $-1/2$ from $M_L = 0$, and $M = -1/2$ and $-3/2$ from $M_L = -1$. We know that if spin-orbit interaction is introduced into the atomic problem, we shall have two energy levels, $^2P_{3/2}$, with $M = 3/2, 1/2, -1/2$, and $-3/2$, and $^2P_{1/2}$, with $M = 1/2, -1/2$. It seems reasonable to suppose that the cubic field will not remove this degeneracy, and that the four-dimensional irreducible representation of T_d will correspond to the $^2P_{3/2}$ atomic state, and the additional two-dimensional representation to $^2P_{1/2}$. Let us then use this hint to try to set up basis functions and hence the matrix elements of the irreducible representations.

Let us start with the $^2P_{3/2}$. We can set up the basis functions corresponding to $M = 3/2, -3/2$, as in the earlier cases of C_{3v} and C_{4v} , by combining the spin α with an orbital function corresponding to an orbital angular momentum of 1 unit along the z axis, and combining β with an orbital function with angular momentum -1. Since we are taking the z axis as the axis of quantization, an orbital p function with angular momentum 1 along the axis has a wave function $x+iy$ times a function of r , and that with an angular momentum -1 has a wave function $x-iy$ times the function of r . Hence for the basis functions corresponding to $M = 3/2$ and $-3/2$ we may reasonably expect to use $(x+iy)\alpha$ and $(x-iy)\beta$. These are entirely analogous to the functions ψ_1 and ψ_2 of Eq. (44). We next need functions corresponding to $M = 1/2$ and $-1/2$. We can find these by using atomic vector-coupling methods, coupling the orbital angular momentum of unity with the spin angular momentum of $1/2$ unit. When we do so, we not only find the functions corresponding to $^2P_{3/2}$ for $M = 1/2$, but also the functions for $^2P_{1/2}$. We find the following basis functions:

Basis functions for ${}^2P_{3/2}$

$$\psi_1, M = 3/2: (x+iy)a$$

$$\psi_2, M = 1/2: za - \frac{x+iy}{2} \beta$$

$$\psi_3, M = -1/2: z\beta + \frac{x-iy}{2} a$$

$$\psi_4, M = -3/2: (x-iy) \beta$$

Basis functions for ${}^2P_{1/2}$

$$\psi_1, M = 1/2: za + (x+iy) \beta$$

$$\psi_2, M = -1/2: -z\beta + (x-iy)a \quad (52)$$

We can now use these functions and investigate the operations of the double group T_d on them. We find that they form in fact basis functions for a four-dimensional and an additional two-dimensional irreducible representation, and we find matrix elements as given in Table 9. The basis functions of Eq. (52) are odd on inversion. Hence if we use them to form basis functions for irreducible representations of O_h , the matrix elements and characters for the primed operations are the negatives of those for the unprimed operations. We must find as well basis functions for the other irreducible representations of O_h which will be even on inversion. We must also find basis functions for the two-dimensional irreducible representation of O_h which has the same matrix elements as that of Table 6 but which is odd on inversion. When we do so, we have the following complete set of basis functions for the extra irreducible representations of the double group of O_h , together with the notations used by Koster for these representations:

$$\Gamma_6^+: a, \beta$$

$$\Gamma_7^+: xya + (yz+ixz)\beta, -xy\beta + (yz-ixz) a$$

$$\Gamma_8^+: (yz+ixz)a, xya - \frac{yz+ixz}{2} \beta, xy\beta + \frac{yz-ixz}{2} a, (yz-ixz) \beta$$

$$\Gamma_6^-: za + (x+iy) \beta, -z\beta + (x-iy)a$$

$$\Gamma_7^-: xyza, xyz\beta$$

$$\Gamma_8^-: (x+iy)a, za - \frac{x+iy}{2} \beta, z\beta + \frac{x-iy}{2} a, (x-iy)\beta \quad (53)$$

Table 9

Matrix elements for irreducible representations Γ_7^+ , Γ_8^+ , Γ_6^- , and Γ_8^- of the double group O_h . Basis functions are given in Eq. (53). Matrix elements for the barred operations are negatives of those for the unbarred. Matrix elements for the primed operations equal those of the unprimed for Γ_7^+ and Γ_8^+ , while for Γ_6^- and Γ_8^- they are negatives of those for unprimed. Representations Γ_7^+ and Γ_6^- are on this page, Γ_8^+ and Γ_8^- on the following pages. Table below lists in order the 11, 21, 12, and 22 matrix elements and characters.

R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}	R_{16}	R_{17}	R_{18}	R_{19}	R_{20}	R_{21}	R_{22}	R_{23}	R_{24}
1	0	0	1	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1-i}{2}$	0	0
0	1	-1	0	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	0	0	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1-i}{2}$
0	1	1	0	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	0	0	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1-i}{2}$
1	0	0	-1	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	0	0
2	0	0	0	1	1	1	1	1	1	1	1	$-\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	0	0	0	0	0	0

N_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}	R_{16}	R_{17}	R_{18}	R_{19}	R_{20}	R_{21}	R_{22}	R_{23}	R_{24}
11	1	0	0	-1	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1+i}{4}$	$-\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	0	0
21	0	0	0	0	$-\frac{1+i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$\frac{1+i}{2}$	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$-\frac{1-i}{2}$	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0
31	0	0	0	0	$\frac{1+i}{2}$	$\frac{1-i}{2}$	$\frac{1-i}{2}$	$-\frac{1+i}{2}$	$-\frac{1-i}{2}$	$-\frac{1-i}{2}$	$-\frac{1+i}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0
41	0	1	0	0	$-\frac{1+i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$\frac{1-i}{4}$	$-\frac{1+i}{4}$	$\frac{1+i}{4}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$
12	0	0	0	0	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1-i)$	$-\frac{3}{4\sqrt{2}}$	$-\frac{3}{4\sqrt{2}}$	$-\frac{3}{4\sqrt{2}}$	0	0	0	$-\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	0	0
22	1	0	0	1	$-\frac{1+i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1+i}{4}$	$-\frac{1+i}{4}$	$-\frac{1-i}{4}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1-i}{\sqrt{2}}$	$-\frac{1+i}{\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	0	0
32	0	-1	1	0	$\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1+i}{4}$	$\frac{1+i}{4}$	$-\frac{1-i}{4}$	$\frac{1-i}{4}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	0	0	$\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1+i}{\sqrt{2}}$	$\frac{1-i}{\sqrt{2}}$
42	0	0	0	0	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1-i)$	$-\frac{3}{4\sqrt{2}}$	$-\frac{3}{4\sqrt{2}}$	$-\frac{3}{4\sqrt{2}}$	0	0	0	$-\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	0	0
13	0	0	0	0	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1-i)$	$-\frac{3}{4\sqrt{2}}$	$-\frac{3}{4\sqrt{2}}$	$-\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	0	0	$-\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	$\frac{3}{4\sqrt{2}}$	0	0
23	0	-1	0	-1	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$\frac{1+i}{4}$	$-\frac{1+i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1+i}{\sqrt{2}}$	$-\frac{1-i}{\sqrt{2}}$
33	1	0	0	-1	$-\frac{1-i}{4}$	$-\frac{1+i}{4}$	$-\frac{1+i}{4}$	$-\frac{1-i}{4}$	$-\frac{1-i}{4}$	$\frac{1-i}{4}$	$-\frac{1+i}{4}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1+i}{\sqrt{2}}$	$-\frac{1-i}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$-\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0
43	0	0	0	0	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1-i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1+i)$	$\frac{3}{8}(1-i)$	$-\frac{$											

[illegible]

We see that the basis functions of Eq. (52) are those for Γ_8^- and Γ_6^- respectively.

8. Double Point Groups and Double Space Groups

It is not the intention of this note to go thoroughly into the treatment of double space groups. However, we have gone far enough with the double point groups so that the reader should have no trouble reading the literature on the double space groups, or in extending the methods described here to that problem. We shall indicate in this section some of the simpler aspects of the problem. We shall illustrate by a familiar example, the splitting of the three-fold degenerate p-like state at the point Γ in the body- or face-centered cubic structures, by spin-orbit interaction.

It is obvious in the first place how to set up the operations of the double space groups. We combine the translations with the double point groups of operations. Both an operator R and \bar{R} will have identical effects on a function of coordinates, but their effects on the spin functions α and β are identical with what we have found in this note. Hence if we have a function of coordinates and spin, made up as we have indicated here by multiplying a function of coordinates and a spin function, we can find the effect of any operator of the space group on this function. We can set up the multiplication table of the double space group, as we have done for the double point group in this note, and for the single space groups in earlier contributions to the Quarterly Progress Reports. We can then deduce the irreducible representations, using simple basis functions suggested by the single groups, and can find their matrix elements.

Once we have found the irreducible representations and their matrix elements, we can set up basis functions by the method of projection operators. In particular, if we are dealing with a crystal problem, we naturally start with a plane wave multiplied by a spin function α or β , and apply the projection operator technique to this function. The result will be a symmetrized plane wave, combined with a suitably symmetrized spin function. If the matrix elements of the irreducible representations are set up like those using the basis functions of C_{Nv} , when that group forms the group of the wave vector, the spin function arising from the projection operator will ordinarily be quantized along the reduced wave vector. We can illustrate this by a simple example. We have seen in Eq. (51) that there is a parallelism between the operators $X_0, X_1, X_{-1}, Y_0, Y_1, Y_{-1}$ of the group C_{3v} , and the operators $R_1, R_9, R_5, R_{23}, R_{21}, R_{19}$ of the group O_h or T_d . These operators form the group of the wave vector along the direction A , the 111 direction in the cubic crystal. If we use the matrix elements for C_{3v} given in Table 2 (changing the sign of the matrix elements of Y_0 according to Section 6), and form projection operators from these matrix elements, using the two-dimensional irreducible representation of C_{3v} , and allow these projection operators to operate on α , we find that the resulting two basis functions produced

by the projection operators point along the 111 and -111 directions, as determined by the methods of Section 4. Similar results are found in other cases.

From the character tables of the irreducible representations of the groups of the wave vectors in the various directions, we can deduce the compatibility relations in the usual way. Let us now consider in detail the situation at Γ in a cubic crystal, and in the directions Δ , A , and Σ along the 100, 111, and 110 directions respectively. We have seen in Eq. (53) a set of basis functions for the point Γ in a cubic crystal. The representation Γ_6^+ , as we see from this, is the one resembling the $^2S_{1/2}$ state in an atom; its basis functions are the spin functions α and β , the orbital part of the function being totally symmetric. We have noted that we have a similar two-dimensional irreducible representation for every double group, and for the directions Δ and A these representations are called Δ_6 and A_6 respectively, which are obviously compatible with Γ_6^+ .

In addition to this two-dimensional irreducible representation of the groups C_{4v} and C_{3v} , met in Δ and A respectively, we recall that for C_{4v} we have another two-dimensional irreducible representation, with basis functions (provided we are taking the wave vector along z) of the form $(x+iy)\alpha$, $(x-iy)\beta$. This representation is called Δ_7 . It then proves to be the case, as we can prove from the character tables, that Γ_6^+ and Γ_6^- are compatible with Δ_6 , Γ_7^+ , and Γ_7^- with Δ_7 , and Γ_8^+ and Γ_8^- with both Δ_6 and Δ_7 . Similarly we recall that for C_{3v} there are two one-dimensional irreducible representations, called A_4 and A_5 , in addition to the two-dimensional representation A_6 . It then proves to be the case that Γ_6^+ , Γ_6^- , Γ_7^+ , and Γ_7^- are all compatible with A_6 , while Γ_8^+ and Γ_8^- are compatible with A_4 , A_5 , and A_6 . Since there is only one irreducible representation of C_{2v} , the group of the wave vector along Σ , namely the two-dimensional representation with basis functions α and β , this is compatible with all of the irreducible representations at Γ .

Let us now look more closely at the physical meanings of these representations and compatibilities. An atomic S state will go in the crystalline field into the irreducible representation Γ_6^+ , as we have seen, with the basis functions α and β . This is compatible along each of the three symmetry directions in which the basis functions again are α and β , or two linear combinations of these. An atomic P state on the other hand will be split into the two-dimensional irreducible representation Γ_6^- and the four-dimensional Γ_8^- , as we can see at once from the basis functions of Eq. (53). In our earlier discussion we have seen that the Γ_6^- is analogous to the atomic state $^2P_{1/2}$, and the Γ_8^- to $^2P_{3/2}$. The two states will of course be split apart by spin-orbit interaction. Along the direction Δ Γ_6^- will be compatible with Δ_6 , while Γ_8^- will be compatible with Δ_6 and Δ_7 . Since these two two-dimensional irreducible representations will have different energies, we see that the four-dimensional $^2P_{3/2}$ -like state at Γ will be split

into two two-dimensional states along the direction Δ . In the direction Λ it will likewise be split into two two-dimensional states: we have compatibility with Λ_4 , Λ_5 , and Λ_6 , but we remember that the two one-dimensional irreducible representations Λ_4 and Λ_5 are degenerate on account of time reversal.

In each case of these directions Δ and Λ , one of the two-dimensional representations with which Γ_8^- is compatible has the basis functions α and β , and corresponds to a component of angular momentum along the reduced wave vector $\pm 1/2$. The other, however, has basis functions like $(x+iy)\alpha$, $(x-iy)\beta$, with corresponding functions for the direction Λ , corresponding to components of angular momentum along the reduced wave vector of $\pm 3/2$. The orbital functions set up by projection operators, in the form of symmetrized plane waves, will have the same symmetry properties as $x \pm iy$, etc., about the lattice points. For instance, for a simple cubic lattice of spacing a , basis functions for Δ_7 are

$$e^{ikz} \left[\sin \frac{2\pi h_1 x}{a} \cos \frac{2\pi h_2 y}{a} \pm i \cos \frac{2\pi h_2 x}{a} \sin \frac{2\pi h_1 y}{a} \right] \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

where h_1, h_2 are integers.

The reason, of course, for using the basis functions of the irreducible representations of the double group is that the Hamiltonian, including spin-orbit interaction, commutes with the operators of this double group, and consequently there will be no non-diagonal matrix elements of the Hamiltonian, including spin-orbit interaction, between basis functions for different irreducible representations of the double group. This fact then will be used in solving the problem of spin-orbit interaction in solids. Suppose, for example, that we had solved the problem of energy bands in a crystal, with neglect of spin-orbit interaction, using the irreducible representations of the single group. Suppose then that we wish to introduce the spin-orbit interaction as a perturbation. We may take the basis functions of the irreducible representations of the single group, multiply these by spin functions α or β , or by the appropriate spin functions pointing along the reduced wave vector, and construct from them basis functions for the irreducible representations of the double group.

The commonest case is the one which we have been using as an illustration, the splitting of a p-like irreducible representation of the single group by spin-orbit interaction. From Eq. (53) it is clear how to set up basis functions at Γ . The spin-orbit interaction will be diagonal with respect to these states. When we are not far from the point Γ , and have small splitting between the components of this p-like state, we may disregard non-diagonal matrix elements of the spin-orbit interaction between these components and any other energy levels. Along the direction Δ , then we have seen that we shall have two

states Δ_6 , one arising from each of the energy levels at Γ , and one Δ_7 . Obviously we shall have to consider the interaction between the two Δ_6 's. There will be a non-diagonal matrix element of the spin-orbit interaction between them, proportional to the reduced wave vector, leading to a quadratic secular equation. Similarly in the direction A, we shall have Δ_4 , Δ_5 , and two Δ_6 's, between which we must solve a quadratic secular equation.

It is hoped that this description of some of the simpler procedures for dealing with the double groups will give the reader enough familiarity with their manipulation so that he can proceed to the more complicated cases often met in practice.

References

1. G. F. Koster, Space Groups and their Representations, Solid State Physics, Vol. V, Academic Press, Inc., 1957.
2. E. P. Wigner, Group Theory and its Application to the Quantum Mechanics of Atomic Spectra, Academic Press, Inc., 1959, pp. 154, 167, 357-359.
3. See for instance J. C. Slater, Quantum Theory of Atomic Structure, Volume 2, McGraw-Hill Book Co., Inc., 1960, Sec. 19-4.
4. J. C. Slater, Quantum Theory of Molecules and Solids, Volume 1, McGraw-Hill Book Co., Inc., 1963, Chapter 8. Also Quarterly Progress Report No. 46, Solid-State and Molecular Theory Group, M.I.T., October 15, 1962, p. 68.
5. J. C. Slater, Quantum Theory of Atomic Structure, Volume 2, McGraw-Hill Book Co., Inc., 1960, Chapter 23.
6. E. P. Wigner, Nachr. kgl. Ges. Wiss. Göttingen Math.-phys. Kl. p. 546 (1932); see also Koster, Ref. 1.

ENERGY BANDS IN NICKEL OXIDE

A. C. Switendick

I. Introduction

It has been some time since our last report on the subject of the energy bands in nickel oxide and considerable progress has been made in the interlude. This report will give our results to date and our conclusions regarding nickel oxide.

II. Preliminary Considerations

The augmented plane wave method (hereafter called the APW method) was originally proposed by Slater¹. Calculations of the band structure of iron have been made by Wood² using the APW method as programmed by him for the IBM 709 computer. These computer programs have been extended to include structures containing two atoms in the unit cell, in particular for the sodium chloride structure which non-magnetic nickel oxide possesses. There are several considerations to be made before initiating an APW calculation. These considerations are: (1) choice of potential, (2) choice of APW sphere radius (within which the potential is assumed spherically symmetric), (3) choice of the value of the constant potential assumed to exist outside the spheres, and (4) choice of the ionicity of each of the atoms in the unit cell.

We shall consider the ionicity first. The atomic configuration of nickel is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^8(4s)^2$ and that of oxygen is $(1s)^2(2s)^2(2p)^4$. Chemical concepts of valence would lead to the ions Ni^{+2} and O^{-2} , with the outer electronic configurations of $(3d)^8$ and $(2p)^6$ respectively. Crystalline field theory for nickel oxide gives good interpretation of experiment with the assumption of the ground state of the nickel ion as $(d_x)^6(d_y)^2$, where d_x corresponds to combinations of atomic d-functions to yield localized functions xy , xz , yz and d_y to $3z^2-r^2$, and x^2-y^2 . On these bases we have

assumed the ionicities of +2 for nickel and -2 for oxygen. The APW method requires a spherically symmetric potential within the APW sphere containing an ion. The average of the electrostatic field from the other ions in the crystal gives the usual Madelung potential. With the Madelung constant for the sodium chloride structure and the lattice constant a , (nickel-nickel distance along the cube edge of 4.1946 Angstroms compared with 3.517 for nickel metal) and the assumed ionicity, this potential is ± 1.76364 Rydbergs. This value is subtracted from the nickel potential and added to the oxygen potential (taking potential in the ordinary electrostatic sense for positive test charges). The effect of the Madelung potential is to raise all the electronic energy levels associated with the nickel ion and to lower the levels associated with the oxygen ion. Thus the ionicity can affect the energy band structure greatly. The ionicity remained constant in all our investigations. From the energy band results and the band wave functions, we can test the validity of the choice of ionicity.

We next consider the choice of potential to use within the nickel sphere and within the oxygen sphere. Watson^{3, 4} has made analytic Hartree-Fock calculations for Ni^{+2} and O^{-2} . Potentials were constructed using these results. Exchange was included, using the Slater $\rho^{1/3}$ averaged exchange potential⁵. The potential within the n th sphere is given by

$$\begin{aligned}
 V_n(\sigma, r) = & \frac{2Z_n}{r} - \sum_{l, n} \left[\frac{1}{r} \int_0^r P_{nl}^2(r') dr' \right. \\
 & + \int_r^\infty P_{nl}^2(r') \frac{dr'}{r'} \left. \right] + \frac{6}{4\pi} \left[12\pi \sum_{n, l} \frac{N(\sigma, r)}{N(r)} \right. \\
 & \left. \times \frac{P_{nl}^2(r)}{r^2} \right]^{1/3} - V_M - V_O
 \end{aligned} \quad (1)$$

The first three terms represent the spherically averaged coulomb potential of the nucleus and the electrons. The fourth term is the averaged exchange potential where $N(\sigma, r)/N(r)$ is the fraction of the electrons with spin σ at position r . Initially we shall consider non-magnetic nickel oxide and shall take this factor to be 1/2. V_M is the Madelung potential discussed above and V_O is the potential assumed in the region between the spheres and the cell boundary. In Table 1 we give the numerical potential used for non-magnetic nickel oxide.

We now discuss our choice of APW sphere radii. In preliminary investigations we used the ionic radii of Pauling⁶ for oxygen $R_g(\text{O}^{-2}) = 1.40$ Angstroms (2.65 atomic units) and for nickel $R_g(\text{Ni}^{+2}) = .70$ Angstroms

Table 1

Numerical potential used to obtain energy bands for non-magnetic nickel-oxide. Potential used is tabular value - V_{Shift} , where $V_{\text{Shift}} = V_M - V_O$. For oxygen $V_{\text{Shift}} = -.59636$, for nickel $V_{\text{Shift}} = 2.93092$.

r	Oxygen Potential	Nickel Potential	r	Oxygen Potential	Nickel Potential
0.010	1572.57690	5409.38080	0.510	12.25670	33.77772
0.020	771.94769	2609.19739	0.520	11.81944	32.58822
0.030	504.85467	1678.90248	0.530	11.40158	31.45553
0.040	371.25884	1216.50876	0.540	11.00187	30.37616
0.050	291.12782	941.15356	0.550	10.61920	29.34694
0.060	237.76812	759.18992	0.560	10.25254	28.36493
0.070	199.72904	630.53355	0.570	9.90094	27.42744
0.080	171.27809	535.15714	0.580	9.56354	26.53199
0.090	149.22575	461.90842	0.590	9.23954	25.67627
0.100	131.65508	404.06451	0.600	8.92822	24.85814
0.110	177.34411	357.33551	0.610	8.62887	24.07561
0.120	105.47681	318.86890	0.620	8.34090	23.32682
0.130	95.48739	286.70442	0.630	8.06370	22.61005
0.140	86.97121	259.45501	0.640	7.79674	21.92366
0.150	79.63131	236.11253	0.650	7.53952	21.26612
0.160	73.24488	215.92618	0.660	7.29157	20.63602
0.170	67.64157	198.32457	0.670	7.05245	20.03199
0.180	62.68899	182.86469	0.680	6.82176	19.45277
0.190	58.28276	169.19741	0.690	6.59911	18.89717
0.200	54.33956	157.04383	0.700	6.38414	18.36404
0.210	50.79209	146.17851	0.710	6.17651	17.85234
0.220	47.58550	136.41744	0.720	5.97591	17.36103
0.230	44.67462	127.60913	0.730	5.78204	16.88918
0.240	42.02197	119.62792	0.740	5.59462	16.43586
0.250	39.59620	112.36895	0.750	5.41337	16.00023
0.260	37.37092	105.74416	0.760	5.23806	15.58148
0.270	35.32374	99.67923	0.770	5.06843	15.17882
0.280	33.43554	94.11111	0.780	4.90427	14.79152
0.290	31.68991	88.98600	0.790	4.74536	14.41889
0.300	30.07266	84.25776	0.800	4.59149	14.06028
0.310	28.57144	79.88659	0.810	4.44248	13.71504
0.320	27.17543	75.83787	0.820	4.29814	13.38259
0.330	25.87512	72.08136	0.830	4.15829	13.06236
0.340	24.66206	68.59033	0.840	4.02277	12.75381
0.350	23.52874	65.34109	0.850	3.89142	12.45641
0.360	22.46841	62.31239	0.860	3.76408	12.16970
0.370	21.47500	59.48515	0.870	3.64062	11.89320
0.380	20.54303	56.84208	0.880	3.52089	11.62647
0.390	19.66750	54.36753	0.890	3.40476	11.36908
0.400	18.84390	52.04730	0.900	3.29210	11.12065
0.410	18.06810	49.86851	0.910	3.18280	10.88078
0.420	17.33635	47.81949	0.920	3.07674	10.64911
0.430	16.64522	45.88971	0.930	2.97380	10.42530
0.440	15.99160	44.06963	0.940	2.87388	10.20902
0.450	15.37263	42.35069	0.950	2.77688	9.99995
0.460	14.78573	40.72515	0.960	2.68270	9.79779
0.470	14.22853	39.18606	0.970	2.59125	9.60226
0.480	13.69890	37.72715	0.980	2.50243	9.41308
0.490	13.19488	36.34278	0.990	2.41616	9.23000
0.500	12.71468	35.02785	1.000	2.33236	9.05276

Table 1 (continued)

r	Oxygen Potential	Nickel Potential	r	Oxygen Potential	Nickel Potential
1.020	2.17183	8.71490	2.020	-0.53592	2.76806
1.040	2.02024	8.39773	0.040	-0.54732	2.72843
1.060	1.87703	8.09964	2.060	-0.55816	2.68985
1.080	1.74168	7.81917	2.080	-0.56845	2.65227
1.100	1.61371	7.55499	2.100	-0.57824	2.61566
1.120	1.49267	7.30588	2.120	-0.58753	2.57997
1.140	1.37814	7.07072	2.140	-0.59636	2.54518
1.160	1.26974	6.84850	2.160	-0.60474	2.51124
1.180	1.16711	6.63829	2.180	-0.61270	2.47812
1.200	1.06990	6.43924	2.200	-0.62025	2.44580
1.220	0.97781	6.25056	2.220	-0.62741	2.41424
1.240	0.89053	6.07154	2.240	-0.63421	2.38343
1.260	0.80780	5.90152	2.260	-0.64065	2.35332
1.280	0.72936	5.73990	2.280	-0.64675	2.32389
1.300	0.65497	5.58612	2.300	-0.65254	2.29513
1.320	0.58439	5.43967	2.320	-0.65802	2.26700
1.340	0.51743	5.30008	2.340	-0.66320	2.23950
1.360	0.45387	5.16691	2.360	-0.66810	2.21259
1.380	0.39355	5.03977	2.380	-0.67274	2.18626
1.400	0.33627	4.91828	2.400	-0.67712	2.16048
1.420	0.28188	4.80211	2.420	-0.68126	2.13525
1.440	0.23022	4.69092	2.440	-0.68517	2.11054
1.460	0.18114	4.58443	2.460	-0.68885	2.08634
1.480	0.13452	4.48236	2.480	-0.69232	2.06263
1.500	0.09022	4.38447	2.500	-0.69558	2.03940
1.520	0.04811	4.29050	2.520	-0.69865	2.01663
1.540	0.00810	4.20025	2.540	-0.70154	1.99431
1.560	-0.02995	4.11351	2.560	-0.70425	1.97243
1.580	-0.06611	4.03009	2.580	-0.70678	1.95097
1.600	-0.10049	3.94981	2.600	-0.70916	1.92993
1.620	-0.13319	3.87250	2.620	-0.71138	1.90928
1.640	-0.16428	3.79801	2.640	-0.71345	1.88903
1.660	-0.19385	3.72619	2.660	-0.71537	1.86915
1.680	-0.22197	3.65690	2.680	-0.71716	1.84965
1.700	-0.24872	3.59003	2.700	-0.71883	1.83050
1.720	-0.27416	3.52543	2.720	-0.72036	1.81171
1.740	-0.29836	3.46302	2.740	-0.72178	1.79326
1.760	-0.32138	3.40267	2.760	-0.72308	1.77514
1.780	-0.34327	3.34429	2.780	-0.72427	1.75734
1.800	-0.36410	3.28779	2.800	-0.72536	1.73986
1.820	-0.38392	3.23307	2.820	-0.72634	1.72269
1.840	-0.40277	3.18006	2.840	-0.72723	1.70583
1.860	-0.42070	3.12868	2.860	-0.72803	1.68925
1.880	-0.43776	3.07884	2.880	-0.72874	1.67297
1.900	-0.45398	3.03049	2.900	-0.72937	1.65696
1.920	-0.46941	2.98355	2.920	-0.72991	1.64123
1.940	-0.48408	2.93797	2.940	-0.73037	1.62577
1.960	-0.49804	2.89369	2.960	-0.73076	1.61057
1.980	-0.51131	2.85064	2.980	-0.73108	1.59563
2.000	-0.52392	2.80878	3.000	-0.73133	1.58094

Table 1 (continued)

Starting Values for Oxygen Potential

l	$P_l (.01)$	$P_l (.02)$
0	0.92278780E-02	0.17018180E-01
1	0.96070194E-04	0.36911326E-03
2	0.97333996E-06	0.75739295E-05
3	0.97965897E-08	0.15339523E-06
4	0.98345038E-10	0.30909043E-08
5	0.98597797E-12	0.62124747E-10
6	0.98778339E-14	0.12468757E-11
7	0.98913746E-16	0.25003229E-13
8	0.99019060E-18	0.50108679E-15
9	0.99103313E-20	0.10038090E-16
10	0.99172246E-22	0.20102945E-18
11	0.99229688E-24	0.40250494E-20
12	0.99278297E-26	0.80576476E-22

Starting Values for Nickel Potential

l	$P_l (.01)$	$P_l (.02)$
0	0.74742711E-02	0.10867903E-01
1	0.86935680E-04	0.30231151E-03
2	0.91000002E-06	0.66125865E-05
3	0.93032162E-08	0.13791529E-06
4	0.94251457E-10	0.28262685E-08
5	0.95064321E-12	0.57431540E-10
6	0.95644937E-14	0.11615760E-11
7	0.96080398E-16	0.23425700E-13
8	0.96419090E-18	0.47153457E-15
9	0.96690043E-20	0.94790202E-17
10	0.96911733E-22	0.19037124E-18
11	0.97096471E-24	0.38206054E-20
12	0.97252791E-26	0.76635164E-22

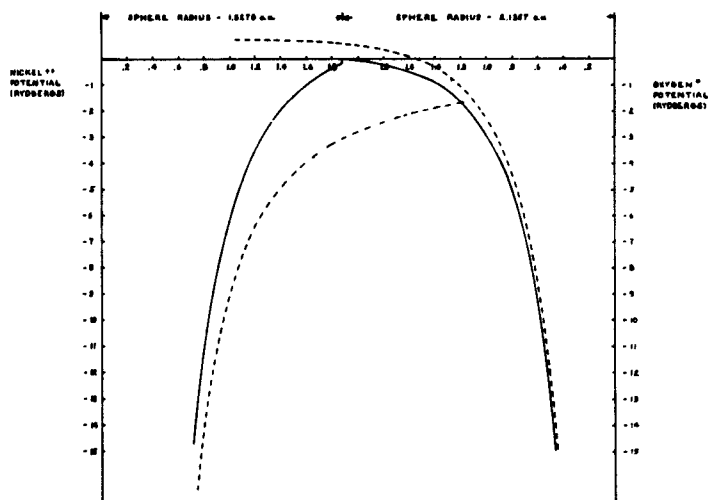


Figure 1. Electronic potential of Table 1 along 1, 0, 0 direction. Dashed curves data of Table 1, solid curves include V_{Shift} .

(1.32 a.u.). These values give $R_s(O^{-2}) + R_s(Ni^{+2}) = 2.10 \approx a/2$. This result is not surprising since these ionic radii were based on the choice of a somewhat arbitrary oxygen radius and the cation radius derived from the appropriate oxide. Convergence of the band states associated with the nickel ion was poor using this choice of sphere radii. We believe that this poor convergence was engendered by the large negative value of the logarithmic derivative at the nickel sphere radius. In order to obtain a solution to Schrodinger's equation with continuous derivative on the surface of the APW sphere, it is necessary to include many plane waves (outside the spheres) with short wavelengths (large wave vector) to achieve this continuity of derivative. Slater⁷ observed that Pauling's ionic radii were somewhat arbitrary and that an equally consistent set of ionic radii could be derived by subtracting a constant from all cation radii and adding this constant to all anion radii. If this constant was chosen such that the sphere radii coincided with a minimum of the combined charge density, then a more physical interpretation of a sphere radius is obtained. The new values of sphere radii obtained in this manner were $R_s(O^{-2}) = 2.1357$ a.u. and $R_s(Ni^{+2}) = 1.8278$ a.u. Since any renormalization of the electronic wave functions would change the radial density and hence the sphere radii, we did not renormalize. This choice of sphere radii using Watson's free ion functions corresponds to 7.52 d-electrons in the nickel sphere and 4.60 p-electrons in the oxygen sphere, and leaves 1.88 electrons in the region outside the spheres. Since this volume, with our choice of sphere radii, is forty-six percent of the unit cell, it does not seem unreasonable to have this much charge in this region. Again the choice of sphere radii can be tested against the charge distribution associated with the bands.

Finally we come to the choice of the value of the zero potential assumed to exist everywhere outside the APW spheres. If we consider the potential along the (1,0,0) direction as shown in Figure 1, we see that there is a discontinuity where the atoms touch. The oxygen potential at the APW sphere radius is -.59636 Rydbergs and the nickel potential is 3.20636 Rydbergs. After the Madelung correction these values are 1.16728 and 1.44272 Rydbergs respectively. In the actual crystal there will be no discontinuity. We could choose the zero potential to be the average value of the discontinuity, but when we consider the relative size of the spheres, we see that the oxygen ion is fifty percent larger than the nickel ion and will more strongly influence the potential between the spheres. We therefore chose the value of the potential at the oxygen sphere to be the zero of potential, or $V_o = 1.16728$ Rydbergs. We also note that for several ionic crystals no appreciable difference would be made in choosing the zero of potential to be the value where the two ionic potentials are equal in the crystal and choosing the sphere radii in this manner. This method of choosing the sphere radii removes the potential discontinuity

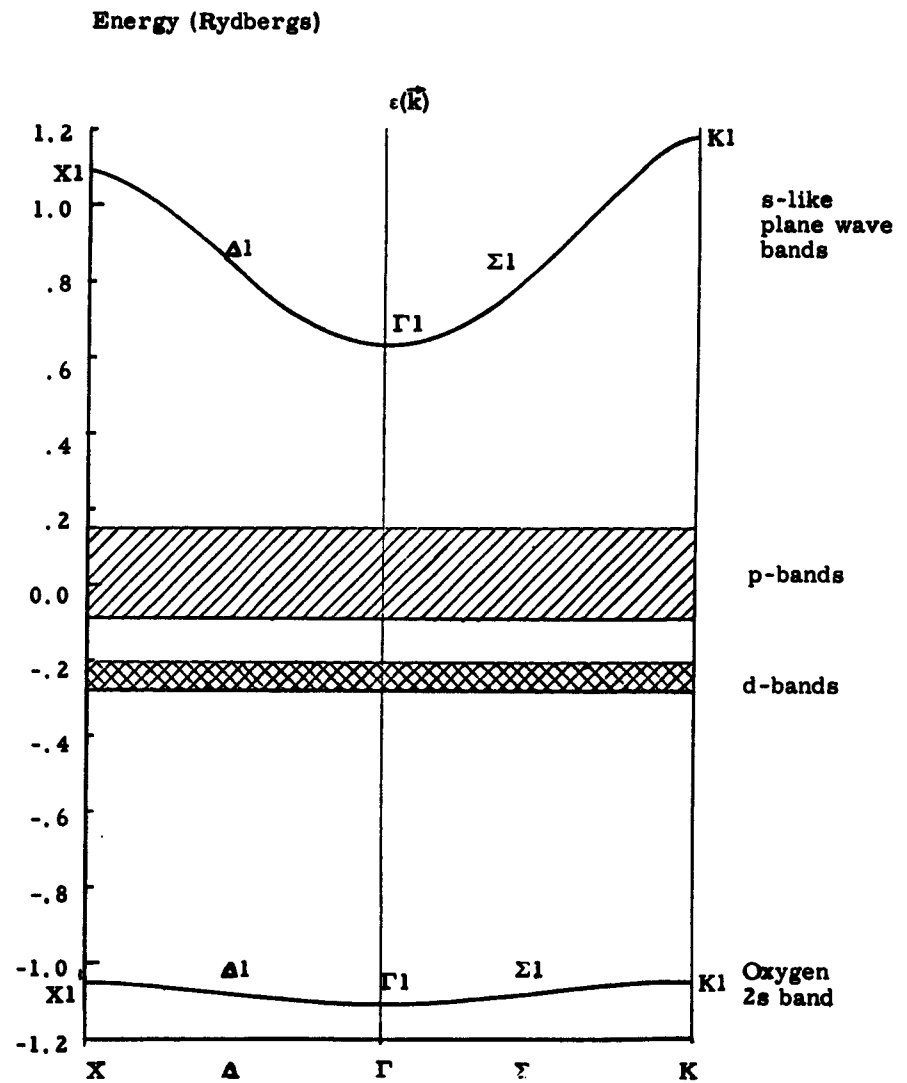


Figure 2. Energy bands for non-magnetic nickel oxide in Δ and Σ direction.

at the spheres, even though this discontinuity does not have much effect on the bands. This concludes our discussion of the preliminaries to an APW calculation.

III. Non-Magnetic Nickel Oxide Band Calculation

Using the potential given in Table 1, energy band states for nickel oxide were calculated. It was found that APW functions with $k^2 \leq (KMAX)^2$ were needed for convergence of the band states to within .001 Rydbergs. The values of $(KMAX)^2$ for the p and d-bands were 64 and 108 (in units of $(\pi/a)^2$) respectively. It was necessary to include terms with l value up to twelve to accurately calculate the matrix elements involved in the secular equation. In Figure 2 we give the results of our energy band calculations for the directions Δ and Σ in the Brillouin zone⁸ for the energy range -1.2 to 1.2 Rydbergs. We note a narrow (.05 Rydbergs) band arising from the 2s-state of oxygen, quite narrow (.08 Rydbergs) bands for the 3d-states of nickel, somewhat wider (.24 Rydbergs) bands for the 2p-state of oxygen, and a wide band (.5 Rydbergs) from s-like states and plane waves (a plane wave band would have a width of .628 Rydbergs). In Figure 3 the detailed results for the energy along the principle symmetry directions in the Brillouin zone are shown. The numerical values from which these curves were derived are given in Table 2. Initially we intended to calculate the energy bands for all points in the Brillouin zone on a mesh of 1/2 (taking the distance from Γ to X as 2 units). This mesh gives 256 points in the zone but for $(KMAX)^2 \leq 108$ it would involve solving large secular equations (80 by 80) for points with only two operations in the group of the wave vector and correspondingly larger ones for groups with only one operation. One such point Q with two representations Q^+ and Q^- was calculated. This involved evaluating a 74 by 74 determinant (for which special programs had to be written) for each representation and took about an hour of computer (IBM 709) time each. For this reason we limited ourselves to a few points of high symmetry in the Brillouin zone.

Since the bands are fairly narrow, the interpolation scheme of Slater and Koster⁹ might be successful in fitting and extending our band structure results to general points in the Brillouin zone. This scheme should ideally work in the case of narrow bands derived from localized atomic wave functions. We therefore investigated the charge density associated with the APW wave functions at the same time as we applied the interpolation scheme. The philosophy of the LCAO scheme is to include only those parameters (interactions) which are necessary to fit the points calculated by a more accurate method such as our APW calculation. One hopes that the number of parameters is smaller than the number of points to be fitted, for the fitting to have any justification.



Table 2

Non-Magnetic Nickel Oxide Energy Band States

We give the value of $\epsilon(\mathbf{k})$ calculated by the APW method. Also given are the values calculated by the LCAO fit. The units of \mathbf{k} are $\frac{\pi}{a}$ where $a = 7.92704$ a.u.

2s Band ($KMAX^2 = 80$)

4k	Symmetry	APW Energy (Rydbergs)
0, 0, 0	Γ_1	-1.1165
0, 2, 0	Δ_1	-1.1055
0, 4, 0	Δ_1	-1.0807
0, 6, 0	Δ_1	-1.0594
0, 8, 0	X_1	-1.0517
2, 2, 0	Σ_1	-1.096
4, 4, 0	Σ_1	-1.06
6, 6, 0	K_1	-1.048

Plane Wave Band ($KMAX^2 = 80$)

4k	Symmetry	APW Energy (Rydbergs)
0, 0, 0	Γ_1	.6249
0, 4, 0	Δ_1	.8346
0, 8, 0	X_1	1.0977
2, 2, 0	Σ_1	.72
4, 4, 0	Σ_1	.965
6, 6, 0	K_1	1.182

ENERGY BANDS IN NICKEL OXIDE

51.

d Bands ($KMAX^2 = 108$)

4k	Symmetry	APW Energy	Fitted Energy
0, 0, 0	Γ_{12}	-. 2278	-. 2278
0, 2, 0	Δ_1	-. 2436	-. 2423
0, 4, 0	Δ_1	-. 2614	-. 2576
0, 6, 0	Δ_1	-. 2375	-. 2350
0, 8, 0	X1	-. 1961	-. 1961
0, 2, 0	Δ_2	-. 2259	-. 2263
0, 4, 0	Δ_2	-. 2226	-. 2227
0, 6, 0	Δ_2	-. 2190	-. 2191
0, 8, 0	X2	-. 2176	-. 2176
0, 0, 0	$\Gamma_{25'}$	-. 2360	-. 2360
0, 2, 0	$\Delta_{2'}$	-. 2380	-. 2383
0, 4, 0	$\Delta_{2'}$	-. 2438	-. 2438
0, 6, 0	$\Delta_{2'}$	-. 2494	-. 2494
0, 8, 0	X3	-. 2517	-. 2517
0, 2, 0	Δ_5	-. 2341	-. 2343
0, 4, 0	Δ_5	-. 2274	-. 2279
0, 6, 0	Δ_5	-. 2176	-. 2174
0, 8, 0	X5	-. 2114	-. 2114
2, 2, 0	Σ_1	-. 2240	-. 2244
4, 4, 0	Σ_1	-. 2142	-. 2151
6, 6, 0	K1	-. 2096	-. 2099
2, 2, 0	Σ_1	-. 2480	-. 2447
4, 4, 0	Σ_1	-. 2667	-. 2635
6, 6, 0	K1	-. 2555	-. 2540
2, 2, 0	Σ_2	-. 2311	-. 2320
4, 4, 0	Σ_2	-. 2222	-. 2228
6, 6, 0	K2	-. 2134	-. 2146
2, 2, 0	Σ_3	-. 2400	-. 2411
4, 4, 0	Σ_3	-. 2450	-. 2454
6, 6, 0	K3	-. 2306	-. 2312

52.

ENERGY BANDS IN NICKEL OXIDE

4k	Symmetry	APW Energy	Fitted Energy
2, 2, 0	Σ_4	-. 2485	-. 2471
4, 4, 0	Σ_4	-. 2670	-. 2635
6, 6, 0	K ₄	-. 2446	-. 2436
2, 8, 0	Z ₁	-. 237	-. 2351
	Z ₁	-. 201	-. 2003
	Z ₃	-. 2245	-. 2246
	Z ₄	-. 2500	-. 2500
	Z ₂	-. 2111	-. 2114
4, 8, 0	W ₁	-. 2012	-. 2015
	W ₂ '	-. 2547	-. 2530
	W ₃	-. 2422	-. 2421
	W ₂	-. 2105	-. 2114
6, 8, 2	Q ₊	-. 216	-. 2173
	Q ₊	-. 254	-. 2547
	Q ₋	-. 213	-. 2166
	Q ₋	-. 257	-. 2560
	Q ₋	-. 267	-. 2657
2, 2, 2	λ_1	-. 2493	-. 2497
	λ_3	-. 2525	-. 2515
	λ_3	-. 2260	-. 2260
4, 4, 4	L ₂ '	-. 2795	-. 2823
	L ₃ '	-. 2734	-. 2715
	L ₃ '	-. 2162	-. 2174

ENERGY BANDS IN NICKEL OXIDE

53.

p Bands ($KMAX^2 = 80$)

4k	Symmetry	APW Energy	Fitted Energy
0, 0, 0	$\Gamma 15$.1017	.1017
0, 2, 0	$\Delta 1$.0878	.0935
0, 4, 0	$\Delta 1$.0432	.0541
0, 6, 0	$\Delta 1$	-.0275	-.0233
0, 8, 0	$X4'$	-.0849	-.0849
0, 2, 0	$\Delta 5$.09655	.0953
0, 4, 0	$\Delta 5$.07905	.0775
0, 6, 0	$\Delta 5$.0570	.0556
0, 8, 0	$X5'$.0449	.0449
2, 2, 0	$\Sigma 1$.0447	.0538
4, 4, 0	$\Sigma 1$.0000	.0048
6, 6, 0	$K1$.0162	.0197
2, 2, 0	$\Sigma 3$.0903	.0878
4, 4, 0	$\Sigma 3$.0432	.0396
6, 6, 0	$K3$	-.0355	-.0366
2, 2, 0	$\Sigma 4$.1317	.1281
4, 4, 0	$\Sigma 4$.1473	.1421
6, 6, 0	$K4$.0943	.0917
2, 8, 0	$Z3$	-.0577	-.0585
	$Z1$.0632	.0667
	$Z4$.02967	.0301
4, 8, 0	$W2'$.07817	.0587
	$W3$	-.0121	-.0095
6, 8, 2	$Q+$.0738	.0732
	$Q-$	-.0285	-.0398
	$Q-$.125	.1216
2, 2, 2	$\lambda 1$.0068	.0133
	$\lambda 3$.1295	.1243
4, 4, 4	$L2'$	-.0455	-.0563
	$L3'$.1521	.1447

One could try to fit the d-bands separately and the p-bands separately, but from the shapes of the bands for $\Delta 1$ and $\Sigma 4$ it is clear that p-d interactions are required. Following the procedure of including only those interactions required to fit all the APW points to within reasonable accuracy, we obtained the parameters given in Table 3. With these fifteen parameters we were able to fit 93 energy levels to within five percent of the band widths. The fitted levels are also given in Table 2. The so-called two-center approximation wherein the fitting parameters obey certain relationships was not found to be quantitatively true for the d-bands, but since in this approximation $\Gamma 12$ and $\Gamma 25'$ are degenerate, we do not even have a one-center approximation. (A two-center approximation in which one has different d-functions for the two states at $k=0$ might indeed be true). Using the fitted bands a density of states was calculated and is shown in Figure 4. The dotted lines indicate the filling of the bands for one electron of each spin per unit cell. Our fitting would indicate the lower band is predominately d-like localized on the nickel and the upper band is predominately p-like localized on the oxygen. Filling these bands with the fourteen electrons in the unit cell, ten (five spin up and five spin down) would fill the lower d-band making neutral nickel and four (two spin up and two spin down) would partially fill the upper p-band making neutral oxygen. Thus we have obtained metallic nickel oxide with an ionicity at variance with our initial assumptions.

To verify that our APW bands do arise from fairly localized charge densities, we investigated the amount of charge density associated with each angular component in each APW sphere and the amount in the plane waves outside the spheres. From the APW solutions we can write

$$Q_{\vec{k},a} = Q_{p.w.}^{\vec{k},a} + \sum_{n=1}^2 Q_n^{\vec{k},a}$$

where $Q_{p.w.}^{\vec{k},a}$ is the charge associated with the plane waves outside the spheres, and $Q_n^{\vec{k},a}$ is the charge in the n th sphere for the representation a of the wave vector \vec{k} . These terms are the result of integrating the APW solutions over the unit cell. Thus

$$Q_{p.w.}^{\vec{k},a} = \int \rho_{p.w.} d\tau \quad \text{outside spheres}$$

$$Q_n^{\vec{k},a} = \int \rho_n^{\vec{k},a} d\tau_n \quad \text{inside } n\text{th sphere}$$

Table 3

Parameters Used to Fit APW Bands

The numerical values used to fit the APW band states, shown in Figure 3, and given in Table 2, are given. The formulas for the matrix elements are given by Slater and Koster in Table II of reference 9. The connection between their parameters and ours is $1 \rightarrow xy$, $2 \rightarrow xz$, $3 \rightarrow yz$, $4 \rightarrow x^2 - y^2$, $5 \rightarrow 3z^2 - r^2$, $6 \rightarrow x$, $7 \rightarrow y$, $8 \rightarrow z$.

Parameter	Value
E11(000)	-.227625
E11(110)	-.00405625
E11(011)	.00098125
E55(000)	-.2120875
E55(110)	.000034375
E44(110)	-.002653125
E66(000)	.02665
E66(011)	-.0045625
E66(110)	.0116625
E61(010)	.021
E85(001)	.05509975
E12(011)	.0012
E15(110)	-.001425
E67(110)	.0160
E61(111)	-.000787031
E64(111)	0.0

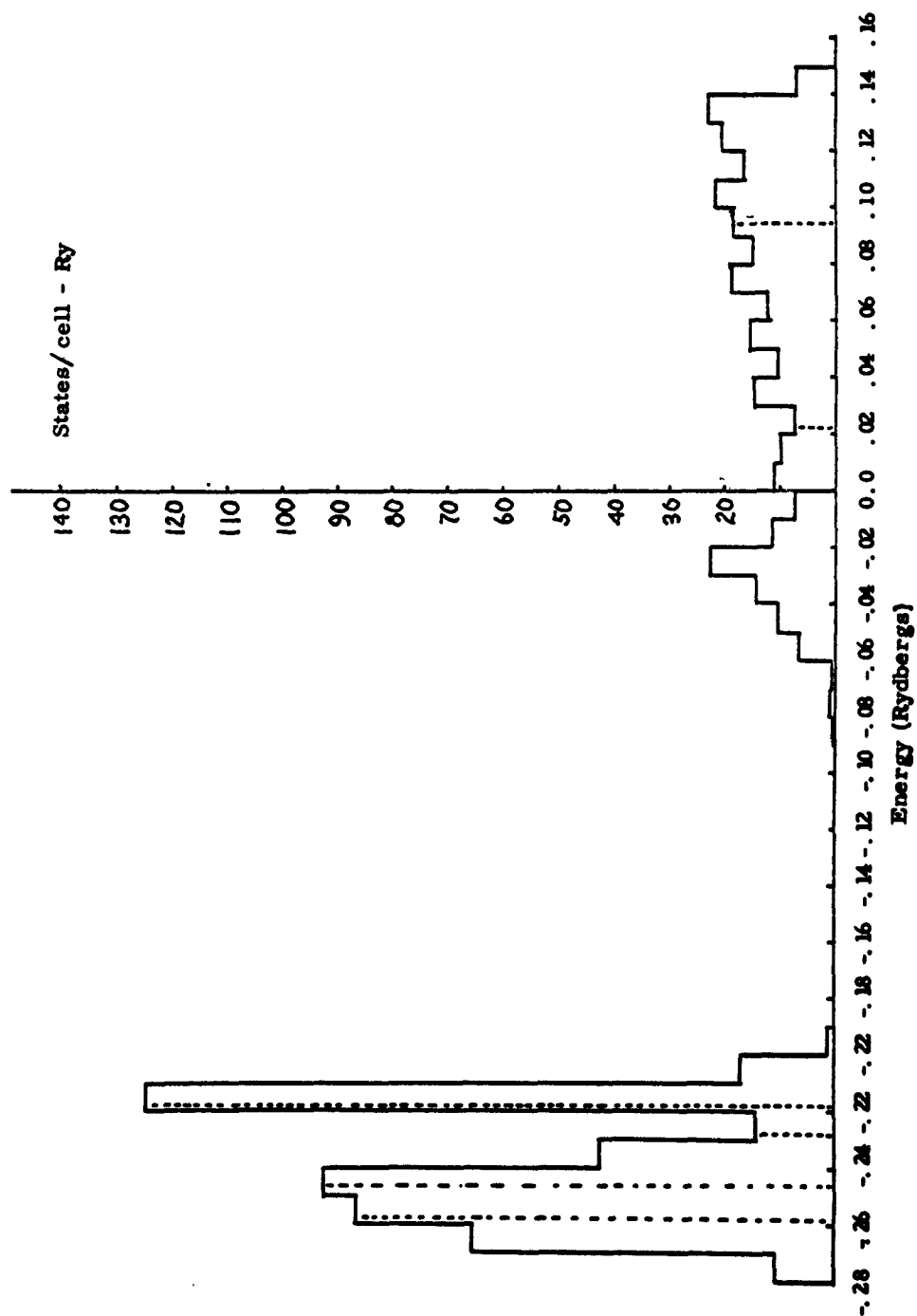


Figure 4. Density of states for non-magnetic nickel oxide derived from fitted APW bands.

We can write

$$\begin{aligned} \rho_n^{\vec{k},a} = & \left(\frac{(l-|m|)!}{(l+|m|)!} \frac{(2l+1)}{\sqrt{8\pi}} \right)^{\frac{1}{2}} u_{n,l}^{\vec{k},a} P_l^{|m|}(\cos \theta) e^{-im\phi} \\ & \times \left(\frac{(l'-|m'|)!}{(l'+|m'|)!} \frac{(2l'+1)}{\sqrt{8\pi}} \right)^{\frac{1}{2}} u_{n,l'}^{\vec{k},a} P_{l'}^{|m'|}(\cos \theta) e^{im'\phi} \end{aligned}$$

If we normalize the total charge distribution to one in the unit cell, we can write

$$\hat{Q}_{p.w}^{\vec{k},a} = Q_{p.w}^{\vec{k},a} / Q^{\vec{k},a}$$

and

$$P_{nl}^2(r) = \frac{u_{nl}^2(r)r^2}{Q^{\vec{k},a}}$$

Then

$$1 = \hat{Q}_{p.w}^{\vec{k},a} + \sum_{n,l} \hat{Q}_{n,l}^{\vec{k},a}$$

where

$$\hat{Q}_{n,l}^{\vec{k},a} = \frac{1}{4\pi} \int_{\text{sphere}} P_{nl}^2(r) dr d\Omega$$

We have evaluated $\hat{Q}_{p.w}^{\vec{k},a}$ and $\hat{Q}_{n,l}^{\vec{k},a}$ for various direction in the Brillouin zone and show these results in Figures 5 through 7. In Figure 5 the amount of oxygen 2p-charge density in the d-bands along $\Delta 1$ varies smoothly from zero percent at $\Gamma 12$ and $X 1$ to sixteen percent inside the zone. However, the percentage of 3d-charge density in the 2p-bands is not so smooth and there is a sizable amount of plane wave in this function. These results manifest themselves in that the $\Gamma 12$ - $\Delta 1$ - $X 1$ states could be fitted very accurately (in fact with quantitative agreement for the wave function) with a simple p-d interaction. This same interaction gave poor fit to the p-bands $\Gamma 15$ - $\Delta 1$ - $X 4'$. Similarly the p-bands could be fitted quite well by a simple p-d interaction (of different magnitude) but the errors were not consistently too high or too low and this fitting gave bad results for the d-bands. The APW wave functions confirm the existence of a p-d interaction which we assumed in order to fit

Percentage in
wave function

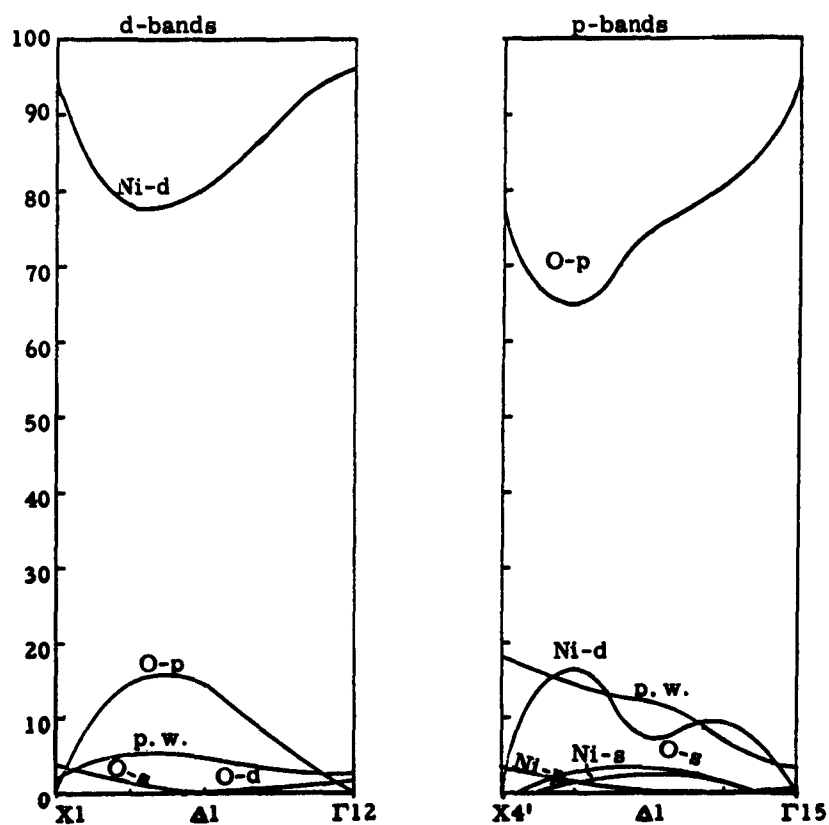


Figure 5. Composition of charge density for d and p-bands with $\Delta 1$ symmetry.

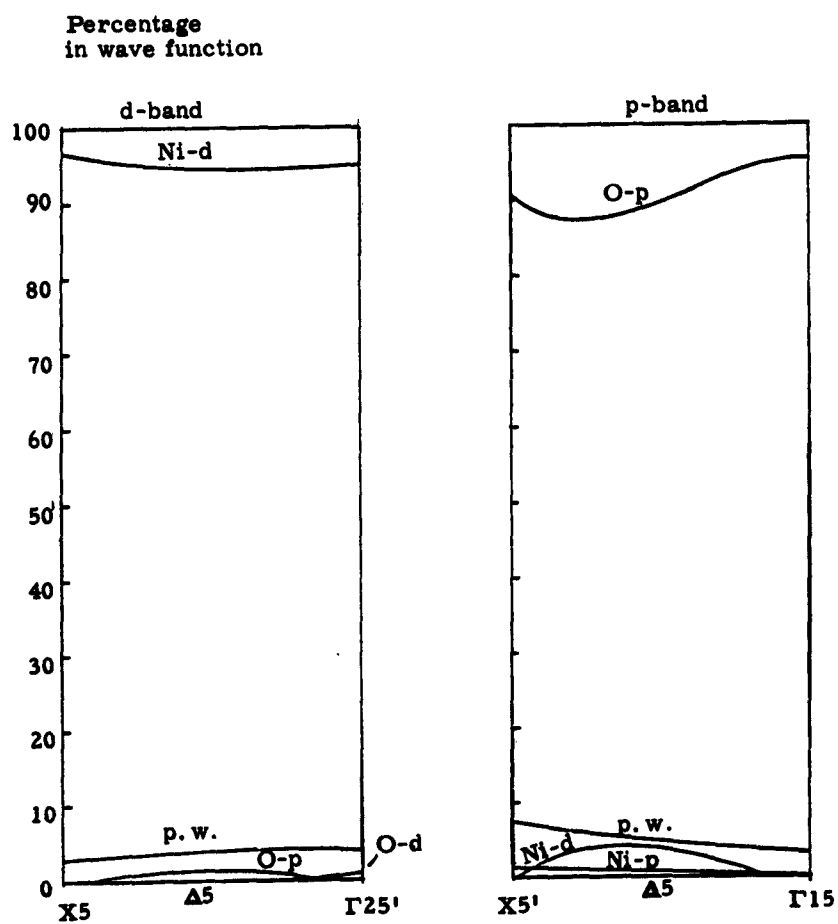


Figure 6. Composition of charge density for d and p-bands with $\Delta 5$ symmetry.

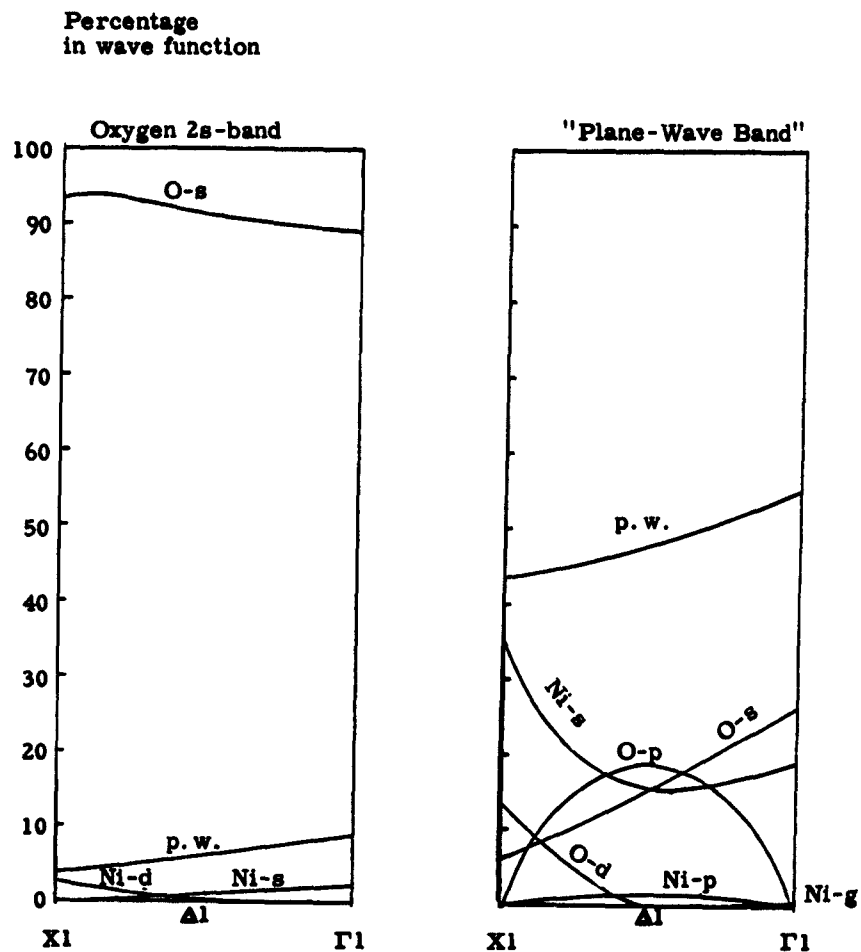


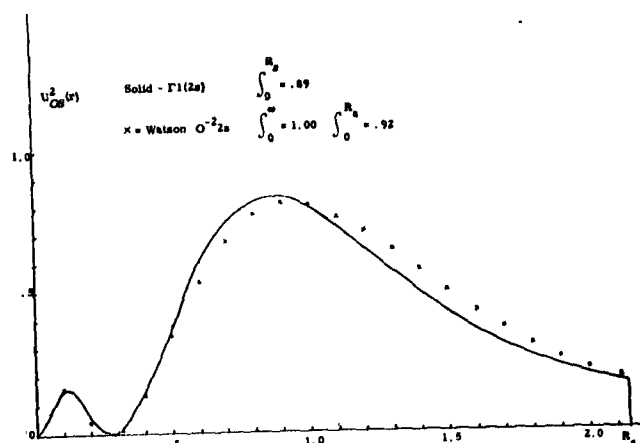
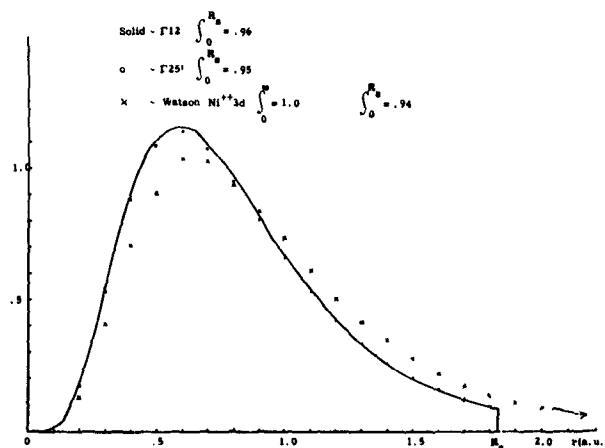
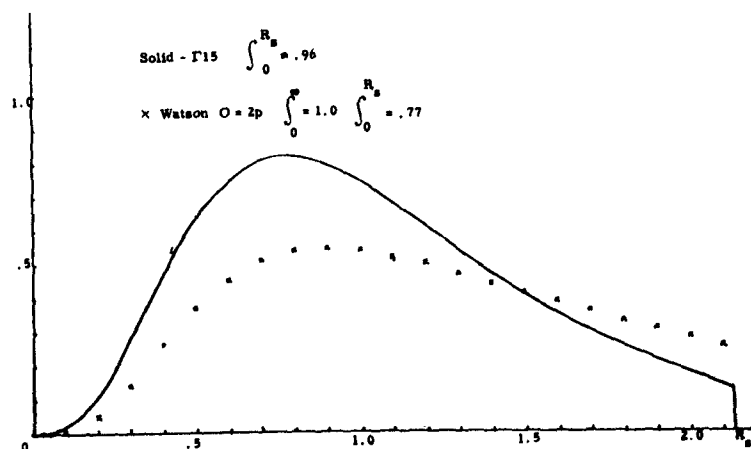
Figure 7. Composition of charge density for 2s and conduction bands with Δ_1 symmetry.

the APW bands. Similar but less dramatic results were found for the symmetry $\Delta 5$ shown in Figure 6. Finally in Figure 7 we show that the oxygen 2s-band is mostly 2s-function with about ten percent plane wave being needed to give continuity of the slope outside the APW sphere. Also in Figure 7 we show the composition of the conduction band which is about half plane wave like and various other distributions as allowed by the symmetry. In Figures 8-10 we show the radial densities associated with the 2s, 3d, and 2p bands. For the 2s-function of Figure 8 the APW function is more contracted than the 2s function of Watson giving three percent more charge inside the sphere, but in quite good agreement with our starting assumption. The 3d-function of $\Gamma 25'$ and $\Gamma 12$ shown in Figure 9 is also in good agreement with Watson's d-function from which our potential was derived. Again the function is more contracted with a few percent more charge in the sphere although this varies according to Figures 5 and 6 as we leave $k=0$. Finally in Figure 10 we show the radial function P_{2p}^2 compared with Watson's function. This time the function is considerably contracted with an increase of twenty percent of an electron inside the sphere for the state $\Gamma 15$. This again decreases according to Figures 5 and 6 as we go away from $k=0$. From Figures 5-10 we conclude that our choice of potential and sphere radius are reasonably consistent but our assumed ionicity of ± 2 turns out to be ± 0 . In the next section we discuss this discrepancy.

The result of our APW energy band calculation for non-magnetic nickel oxide is summarized in Figures 3 and 4. We conclude that filling the lower d-band with ten electrons per cell and partially filling the upper p-band with four electrons per cell gave a charge distribution corresponding to neutral nickel and neutral oxygen at variance with our assumption of Ni^{+2} and O^{-2} . This band structure also gives metallic properties. If we were to do a self-consistent calculation with potentials constructed from our band functions and no Madelung correction, then the new p and d-bands would be separated by three Rydbergs and should be even more localized yielding neutral nickel and neutral oxygen.

IV. Discussion of Non-Magnetic Results and Extension to Antiferromagnetic Structure

In order to obtain the correct ionicity of Ni^{+2} and O^{-2} , it would be necessary to raise two electrons per cell from the d-bands to fill the p-bands. This would still give metallic behavior because of the partially filled d-bands, but would give the correct ionicity. The filling of higher levels in preference to lower ones is similar to the case of atomic nickel $(3d)^8(4s)^2$ where the one-electron 3d-energy is -1.3736 Rydbergs and the one-electron 4s-energy is -.5422 Rydbergs. Yet the 3d level is not completely filled, it being more favorable to allow the 3d-electrons to align their spins to gain "exchange energy" and to fill the higher 4s-states. Callaway¹⁰ gives an expression for the change in the atomic Hartree-Fock potential when one electron reverses its spin as

Figure 8. Radial charge density in oxygen sphere for Γ_1 state.Figure 9. Radial charge density in nickel sphere for $\Gamma_{25'}$ and Γ_{12} states.Figure 10. Radial charge density in oxygen sphere for Γ_{15} state.

$$\frac{1}{7} [F^2(3d, 3d) + F^4(3d, 3d)]$$

Using the integrals evaluated by Watson for nickel (3d)⁸ we obtain

$$\frac{1}{7} [.565 + .909] = .21 \text{ Rydbergs}$$

From the fact that this is about three times the d-band width, we conclude that the magnetic effects are sufficient to split the d-bands into two bands, one for spin up and one for spin down. The separation of these bands being the order of one half a Rydberg. The antiferromagnetic structure of nickel oxide corresponds to two net spins on each nickel site. This antiferromagnetic structure has an Néel temperature of 500°K which corresponds to an energy of .0033 Rydbergs. We would therefore expect the antiferromagnetic band structure to consist of two sets of bands, one set for spin up and the other set for spin down (separated by about .50 Rydbergs) with modifications of each set by splittings of the order of .0033 Rydbergs because of antiferromagnetic effects. Also crystalline field theory would lead us to believe the d-band is split into two sub bands with a gap of about .08 Rydbergs. Barring a complete band structure calculation for antiferromagnetic nickel oxide (face-centered cubic with eight oxygen ions and four spin up nickel ions and four spin down nickel ions in the unit cell), we consider two band structure calculations: one for spin up and the other for spin down (corresponding in some sense to ferromagnetic nickel oxide). Before making such a calculation it seemed wise to compare the location of our bands with the free ion levels in the crystal in order to determine the appropriateness of the $\rho^{1/3}$ exchange potential.

Callaway¹¹ and others have indicated that the use of the free electron or $\rho^{1/3}$ potential may be in error for 3d-bands. The error is in the direction of lowering the 3d-bands and in fact may have erroneously put our d-band below the p-bands (as the results of Morin¹² would indicate). To investigate the reasonableness of the $\rho^{1/3}$ potential we compare the one electron energies for the 2s, 2p, states of oxygen and the 3d states of nickel in the crystal in Table 4. We give the one electron energies from Watson's atomic Hartree-Fock calculations, atomic $\rho^{1/3}$ calculations and the APW band levels at $k = 0$. All levels are quoted relative to the APW zero of energy. From this table we see that the $\rho^{1/3}$ potential is fairly good for the 2p states but is in error by at least .30 Rydbergs for d-functions. We also conclude that the d-level does not shift appreciably in going from the ion into the crystal and the p-level may be considered not to shift but to be broadened by +.14 and -.09 Rydbergs. We see that the error in location of our APW d-bands is due primarily to the use of the $\rho^{1/3}$ approximation for 3d-states.

Table 4

Comparison of eigenvalues for various states in Atomic $\rho^{1/3}$ potential APW calculation and Hartree-Fock calculation.

State	Atomic $\rho^{1/3}$	APW (Γ)	Watson(Shifted)
Ni ⁺² 3d	$-.21460 \pm .00004$	$-.2319 \pm .0041$.10483
O ⁻² 2p	$.0098 \pm .0050$.1017	-.02
O ⁻² 2s	$-1.0512 \pm .0005$	-1.118	-1.408

We have checked that the error in the 3d bands is primarily due to the use of the free electron exchange potential by first order perturbation theory using Watson's atomic functions and atomic potentials

$$\begin{aligned}
 & -[\langle 3d | V_{At}^{H.F.} | 3d \rangle - \langle 3d | V_{At} (\rho^{1/3}) | 3d \rangle] \\
 & = -[3.44 - 3.73] = .29
 \end{aligned}
 \tag{2}$$

which is to be compared with the APW error

$$\epsilon(3d)_{At} - \epsilon(\Gamma_{25'}) = .10 + .23 = .33$$

One could correct for the error in the 3d potential by the use of a screening factor¹³, but this would induce errors in any magnetic effects calculated using this potential. We have found that first order perturbation theory gives very good results for the shift of the APW state at $k = 0$ with a change of potential ΔV , i. e.

$$\epsilon(V)_{k=0} - \epsilon(V)_{k=0} \approx - \langle 3d | \Delta V | 3d \rangle \tag{3}$$

Using equation (1) to calculate a spin dependent potential corresponding to 2.4 spin down electrons (.6 ρ_{3d}) we obtained states at $k = 0$ of $-.0171 \pm .0054$ Rydbergs, a shift of .2148 Rydbergs. The perturbation calculation gave a shift

of .2154 Rydbergs. This corresponds to .135 Rydbergs per spin flip compared with the atomic estimate of .21 Rydbergs. Thus, any screening of the exchange potential (by an exponential-like factor) although improving the non-magnetic energy level location would give poor results for magnetic effects. We have made various calculations using potentials of the form

$$V_{\text{exchg}} = \lambda V_{\text{exchg}} \left(\frac{1}{2} \rho^{\frac{1}{3}} \right) \quad (4)$$

The energy band levels at $k = 0$ are again very well given by the expression (3) (see Table 5). We have also made APW band calculations for nickel oxide using

Table 5

Change in APW eigenvalues for $k = 0$ compared with expectation value of change in potential using atomic 3d functions up to sphere radius.

λ	$\epsilon(\Gamma)_0 - \epsilon(\Gamma)_\lambda$ (Rydbergs)	$-\Delta = (1-\lambda) \langle 3d V(\rho^{\frac{1}{3}}) 3d \rangle$ (Rydbergs)
1.0	0.0	0.0
.929	-.28	-.27
.867	-.52	-.50

the exchange potential of Eq. (4) with $\lambda = .867$. The bands were fitted quite well using the old parameters changing only the location of the states at $k=0$. If we assume the location of the 3d states at $k=0$ to be given by the Hartree-Fock one-electron energies (as a more appropriate Ni^{++} potential would give) and the $\Gamma_{12}-\Gamma_{25'}$ separation to be given by extrapolation from various APW calculations and use the same parameters as obtained for our fitted bands, we obtain the non-magnetic band structure shown in Figures 11-12. Now that the d-bands are above the p-bands, the p-d interaction acts to split the d-bands and prevents the p-bands from rising above $k=0$. These bands are now consistent with Ni^{+2} and O^{-2} . The non-magnetic Fermi level is also shown. These bands however predict metallic behavior. If the $\Gamma_{12}-\Gamma_{25'}$ splitting is taken as $1.06 \text{ eV} \approx .08$ Rydbergs, as crystalline field theory would indicate, the upper band would still be half full giving metallic behavior.

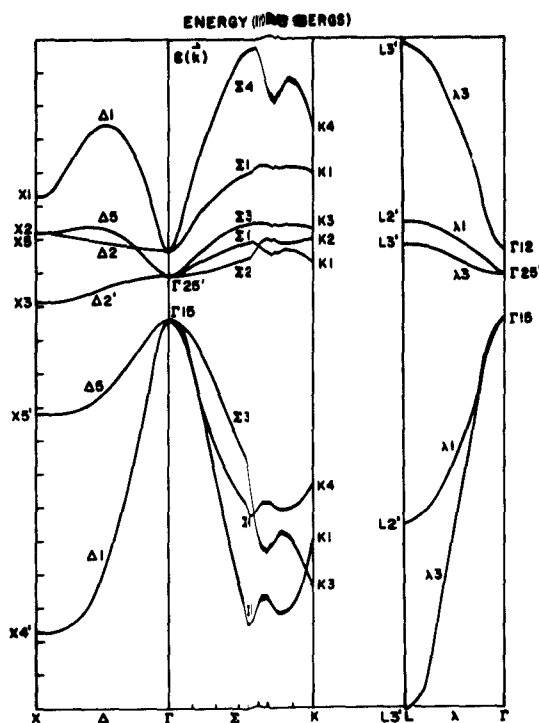


Figure 11. Energy bands for non-magnetic oxide calculated using Hartree-Fock one-electron energies to state Γ_{15} , $\Gamma_{25'}$ and Γ_{12} , and the fitting parameters of Table 3.

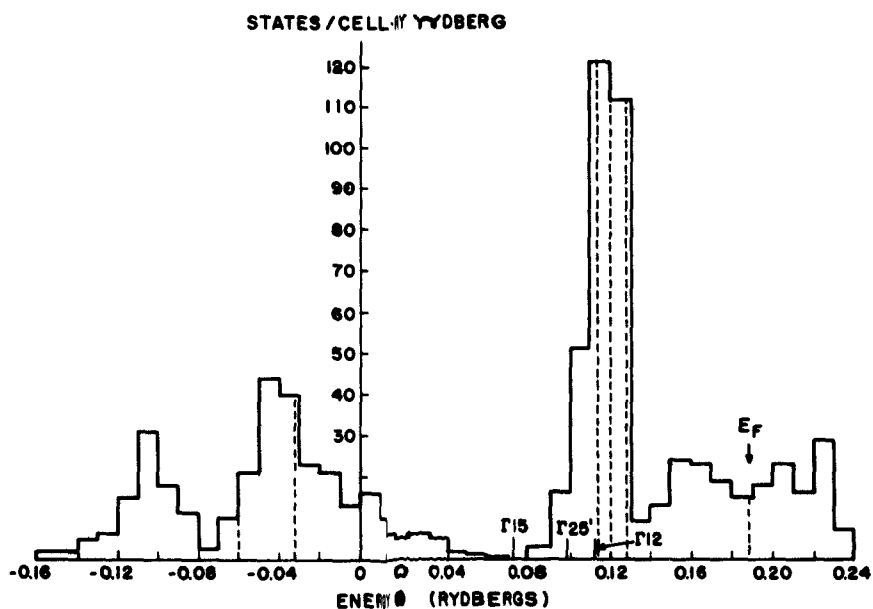


Figure 12. Density of states derived from bands of Figure 11.

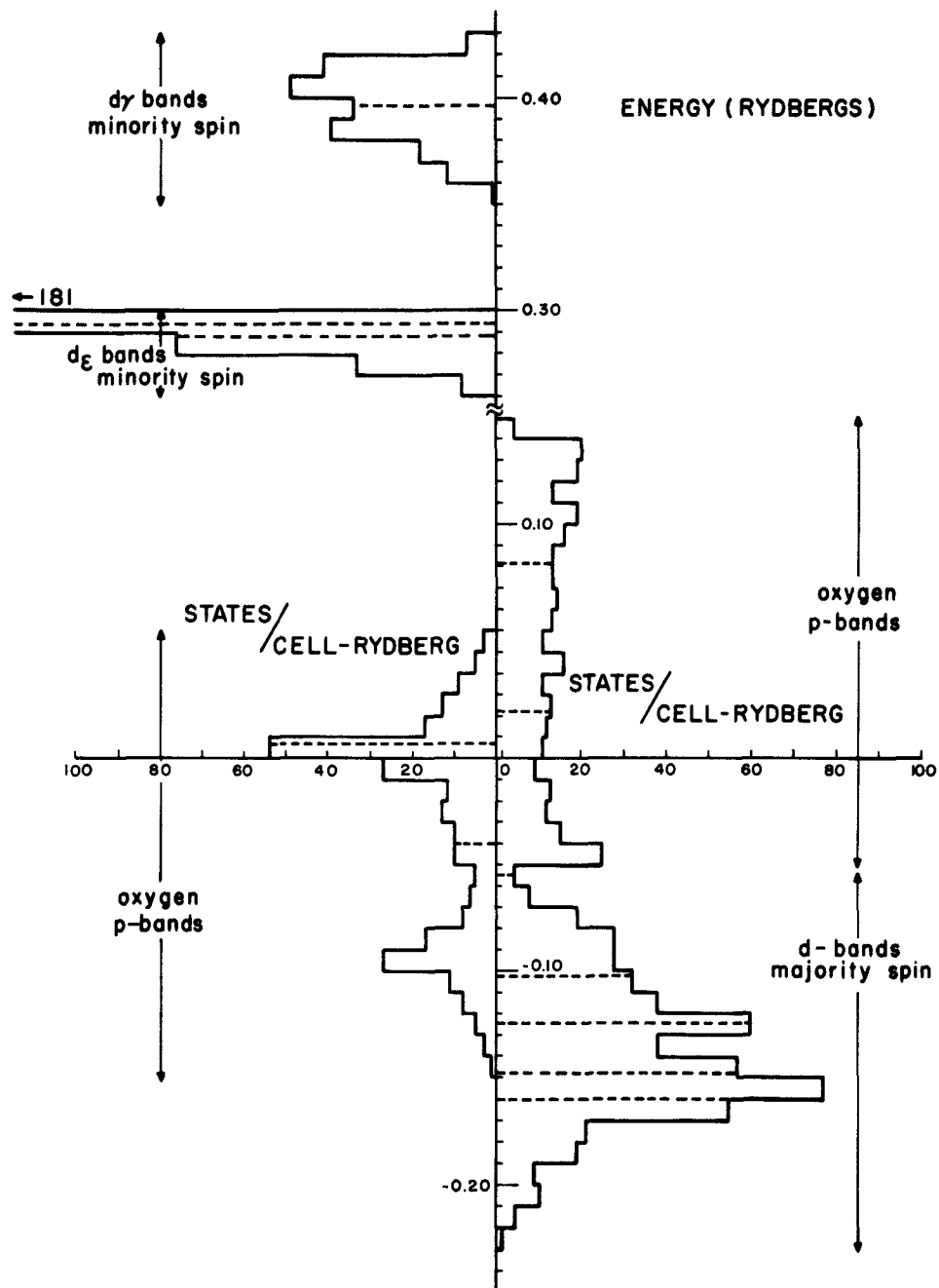


Figure 13. Hypothetical density of states for spin down and spin up bands in nickel oxide including crystalline field splitting of .08 Rydbergs. Note gap in vertical scale.

When we consider the splitting of the d-bands by magnetic effects leading to spin up and spin down bands, we obtain the results shown in Figure 13. These results are both consistent with Ni^{+2} and O^{-2} and, including the crystalline field splitting at $k=0$, gives full d-bands with a gap of .05 Rydbergs. Thus we believe that the insulating properties of nickel oxide are due to the splitting of the d-bands by the different potentials seen by a spin up or spin down electron at every nickel site and the crystalline field splitting of the uppermost d-band into d_{ϵ} and d_{γ} sub-bands. To visualize the result of the antiferromagnetic structure, we would consider the potential seen by a spin up electron at the eight nickel ions in the cell (twice as big in every direction). To first order this would give a structure like Figure 13. where each d-band now corresponds to four bands. The lower set of four corresponds to the 3d up electron located on an up site and the upper set of four bands to the 3d up electron located on the down sites. The reverse picture would hold for a spin down electron on the down sites. Filling the spin up(down) bands with half the electrons in the cell (since there are as many up as down in the cell) would give 5 spin ups (downs) on each up (down) site and 3 spin ups (downs) on each down (up) site. The splitting of the states of the same symmetry probably would be of the order of .0033 Rydbergs and would not remove the gap between the d_{ϵ} and d_{γ} states. This is about as far as we care to speculate barring a more accurate energy band calculation which should include a more accurate 3d potential (probably of the Hartree-Fock type), crystal field effects of non-spherical, non-constant potential at least outside the spheres and the correct antiferromagnetic structure.

References

1. J. C. Slater, Phys. Rev. 51, 846 (1937).
2. J. H. Wood, Phys. Rev. 126, 517 (1962).
3. R. E. Watson, Technical Report No. 12, June 15, 1959, Solid-State and Molecular Theory Group, MIT, Cambridge, Mass., (unpublished).
4. R. E. Watson, Phys. Rev. 111, 1108 (1958).
5. J. C. Slater, Phys. Rev. 81, 385 (1951).
6. L. Pauling, Nature of the Chemical Bond, Cornell University Press, Ithaca, 1945, p. 346.
7. J. C. Slater, MIT Solid-State and Molecular Theory Group Quarterly Progress Report No. 46, October 15, 1961 and private communication.
8. L. P. Bouckaert, R. Smoluchowski, E. Wigner, Fig. 4., Phys. Rev. 50, 65 (1936)
9. J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1959).

10. J. Callaway, Phys. Rev. 99, 500 (1955).
11. Ibid.
12. F. J. Morin, Bell Telephone System Technical Journal 37, 1047 (1958).
13. J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters 9, (1962).

SCF CALCULATIONS ON NEON, USING GAUSSIAN FUNCTIONS

M. C. Harrison

In order to get some idea of the possible accuracy of wavefunctions using Gaussian orbitals, a series of calculations on the ground state of the Neon atom has been completed, using between 9 and 24 basic Gaussians. The restriction that Gaussians of the same symmetry should have exponents in geometric progression so that adjacent functions would have equal overlap, was retained from previous calculations¹. Thus the exponents for a particular symmetry (s or p in this case) could be specified by two parameters β and c , which will be taken to be the exponent of the center Gaussian, and the ratio between adjacent exponents.

The results for the 41 calculations are given in Table I. Atomic units are used throughout. The s functions are of the form e^{-ar^2} , and the p functions of the form $f(x, y, z) e^{-ar^2}$, where $f(x, y, z)$ is x, y, or z. The energy converges fairly slowly towards the Hartree-Fock energy of -128.547 calculated by Clementi² with a basis of two 1s, three 2s, and four independent 2p Slater orbitals.

To give some idea of how critical the choice of parameters is for the various sized bases, an energy surface of the form

$$E = E_0 + P(\beta - \beta_0)^2 + Q(c - c_0)^2$$

was fitted by five points for each pseudo-optimisation. The assumption of independence of β and c implicit in the parabolic fit should be noted as an approximation, as should the assumption of independence of s and p optimisation. It is thought that these assumptions may be justified in view of the present crude optimisation procedure. The results are given in Table II, and show fairly systematic behavior of the parameters. The only anomalous

result seems to be that the choice of c for 3 p functions is as critical as for 2 p functions.

Table III tabulates the values $\frac{P\beta_o^2}{100}$ and $\frac{Qc_o^2}{100}$, which represents the change in E calculated from the energy surface, when the parameters β and c respectively are in error by 10 percent. These figures show the expected result that neither β or c are very critical except for the very small bases, and that c is more critical than β . If the product of $\frac{P\beta_o^2}{100}$ and $\frac{Qc_o^2}{100}$ is taken as a somewhat arbitrary measure of the criticalness of the set, then the resulting order of the sets is 3s(.012), 2p(.0016), 5s(.0013), 3p(.00029), 7s(.00012), 9s(.000026), 5p(.0000072). This suggests that balanced sets would consist of 5s and 2p functions, or 7s and 3p functions, or 9s and 4p functions, a result which seems consistent with calculated total energies.

References

1. C. M. Reeves and M. C. Harrison, J.C.P. July 1963.
2. E. Clementi, J.C.P. 38, 996, 1962.

Table 1. Neon Bases and Energies

Calculation Number	Number of s functions	s exponents	Number of p functions	p exponents	Energy
1	5	.88, 4.4, 22, 110, 550	1	1.0	-123.105
27	3	1.6, 12.8, 102.4	2	.8, 4.0	-122.1899
28	3	.8, 6.4, 51.2	2	.8, 4.0	-119.4131
29	3	3.2, 25.6, 204.8	2	.8, 4.0	-118.3532
30	3	1.28, 12.8, 128.0	2	.8, 4.0	-121.2371
31	3	2.13, 12.8, 77.0	2	.8, 4.0	-121.4427
37	3	1.6, 12.8, 102.4	2	.8, 4.0	-122.1899
32	3	1.6, 12.8, 102.4	2	1.0, 5.0	-122.1668
33	3	1.6, 12.8, 102.4	2	.6, 3.0	-121.9434
34	3	1.6, 12.8, 102.4	2	.7, 4.2	-122.2694
35	3	1.6, 12.8, 102.4	2	.8, 4.8	-122.3240
2	5	.88, 4.4, 22, 110, 550	3	.2, 1.0, 5.0	-127.225
3	5	.88, 4.4, 22, 110, 550	3	.125, 1.0, 8.0	-126.805
4	5	.88, 4.4, 22, 110, 550	3	.4, 1.0, 2.5	-126.150
5	5	.88, 4.4, 22, 110, 550	3	.4, 2.0, 10.0	-127.644
6	5	.88, 4.4, 22, 110, 550	3	.8, 4.0, 20.0	-127.641
7	5	.88, 4.4, 22, 110, 550	3	.6, 2.4, 14.4(!)	-127.598
8	5	.88, 4.4, 22, 110, 550	3	.6, 3.6, 21.6	-127.564
26	5	.88, 4.4, 22, 110, 550	3	.6, 3.0, 15.0	-127.710
37	5	.88, 4.4, 22, 110, 550	3	.6, 3.0, 15.0	-127.710
38	5	1.32, 6.3, 165.825	3	.6, 3.0, 15.0	-127.489
39	5	0.66, 3.1, 5.82, 5.412.5	3	.6, 3.0, 15.0	-127.576
40	5	1.375, 5.5, 22.88, 352	3	.6, 3.0, 15.0	-127.321
41	5	0.611, 3.67, 22.132, 792	3	.6, 3.0, 15.0	-127.425
9	7	.176, .88, 4.4, 22, 110, 550, 2750	3	.6, 3.0, 15.0	-127.996
10	7	.352, 1.76, 8.8, 44, 220, 1100, 5500	3	.6, 3.0, 15.0	-127.887
11	7	.088, .44, 2.2, 11, 55, 275, 1375	3	.6, 3.0, 15.0	-127.837
13	7	.7, 2, 7, 22, 70, 220, 700	3	.6, 3.0, 15.0	-128.079
14	9	.22, .7, 2, 7, 22, 70, 220, 700, 2200	3	.6, 3.0, 15.0	-128.264
15	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	3	.6, 3.0, 15.0	-128.289
16	9	.11, .35, 1.1, 3.5, 11, 35, 110, 350, 1100	3	.6, 3.0, 15.0	-128.192
17	9	.171875, .6875, 2.75, 11, 44, 176, 704, 2816, 11264	3	.6, 3.0, 15.0	-128.222
18	9	.543, 1.629, 4.88, 14.66, 44, 132, 396, 1188, 3564	3	.6, 3.0, 15.0	-128.284
19	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	5	.33, 1.0, 3.0, 9.0, 27.0	-128.490
20	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	5	.1875, .75, 3.0, 12.0, 48.0	-128.487
21	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	5	.48, 1.2, 3.0, 7.5, 18.75	-128.427
22	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	5	.25, .857, 3.0, 10.4, 36.0	-128.501
23	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	5	.5, 1.7, 6.0, 21.0, 72.0	-128.483
24	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	5	.2, .68, 2.4, 8.4, 28.8	-128.499
25	9	.44, 1.4, 4.4, 14, 44, 140, 440, 1400, 4400	5	.33, 1.14, 4.0, 14.48	-128.506

Table II. Parameters of parabolic fits to energy surfaces

Calculations	Functions optimised	Number of functions	Remaining functions	P	ρ_0	Q	c_0	E_0
27, 28, 29, 30, 31	s	3	2p	0.0382	28.8	0.212	7.88	-122.428
37, 38, 39, 40, 41	s	5	3p	0.00269	23.8	.337	5.08	-127.720
9, 10, 11, 12, 13	s	7	3p	0.000588	28.8	0.156	3.94	-128.200
14, 15, 16, 17, 18	s	9	3p	0.000164	36.5	0.111	3.22	-128.299
27, 32, 34, 35, 36	p	2	3s	0.784	1.98	0.144	5.87	-122.327
4, 5, 6, 8, 26	p	3	5s	0.0675	2.99	0.182	5.17	-127.715
19, 20, 22, 24, 25	p	5	9s	0.00833	3.80	0.0498	3.47	-128.506

Table III. Energy changes for 10 percent errors in parameters

Functions	Number of functions	Error in β	Error in c
s	3	.089	.13
s	5	.015	.087
s	7	.0049	.024
s	9	.0022	.012
p	2	.031	.050
p	3	.0060	.049
p	5	.0012	.0060

SCF CALCULATIONS OF HYDROGEN FLUORIDE, USING GAUSSIAN FUNCTIONS

M. C. Harrison

Calculations on the ground state of HF are reported for three bases, each at three internuclear distances near the experimental equilibrium distance of 1.7328 a.u. The bases were chosen to stress the importance of the outer shells (see¹), the fluorine functions comprising 9s and 5p for basis I, 5s and 3p for basis II, and 3s and 2p for basis III. In each case 3 s functions were used for the hydrogen, with a p σ function added for basis I. The exponents for the fluorine were chosen by approximately scaling the exponents used in Neon calculations 25, 26, and 36, reported separately¹. The scale factor was determined by the Slater rules for exponentials, as suggested by Reeves². Thus, to transform Ne exponents to F exponents, the factor for 1s should be $(\frac{8.7}{9.7})^2$, and for 2s and 2p should be $(\frac{8}{9})^2$. These are both close to 0.8, which was in fact used. The actual exponents are given in Table 1.

The total energies, orbital energies, and dipole moments for the nine calculations are given in Table 2, with the same results for calculations by Clementi³ and Ransil⁴. Atomic units are used throughout. Clementi estimates that his total energy is within .005 of the true Hartree-Fock energy, so comparison with his results will be taken as an indication of accuracy. It is seen that the energies for calculations III, II, I, at 1.75, converge monotonically to Clementi's. If we assume that this rather surprising result suggests that in this context the accuracy of the orbital energy provides an indication of the accuracy of the orbital, it is seen that Ransil's minimal Slater basis is inferior to basis II except for 1 σ and total energy, and is superior to basis III except for 1 σ . These conclusions are consistent with previous indications¹ that balanced atomic bases should have 9s + 4p, or 7s + 3p, or 5s + 2p functions, and also with the closeness of Ransil's total energy with that of basis II.

Parabolic interpolation gives equilibrium internuclear distances of 1.74 for bases I and II, identical with the values obtained by Clementi and Ransil. The inability of basis III to give an equilibrium distance in the correct range would seem to indicate some serious deficiency in the wavefunction. Further evidence is necessary to determine just what this is, but comparison of orbital energies with Ransil's values suggest that the inner shells are responsible.*

The values obtained for dipole moments are rather discouraging. Again there is monatomic variation, but to a value which is too high. However, it may be that the addition of p_H and d_F orbitals, as used by Clementi, would effect the improvement. It should be noted that the SCF procedure was terminated when the total energy agreed to within .00001 in all cases, resulting in about 3 significant figures in the density matrix. It is not clear how accurate a dipole moment can be calculated from such a density matrix, but consideration of the values for different internuclear distances suggests that at least one or two figures are significant.

References

1. M. C. Harrison, MIT, SSMTG, QPR (this issue).
2. C. M. Reeves, JCP, July, 1963.
3. E. Clementi, JCP, 36, 33, 1962.
4. B. J. Ransil, RMP, 32, 239, 1960, and JCP 35, 669, 1961.

* It is seen that the occupied orbital energies increase monotonically with increasing internuclear distance with the exception of 1σ , with qualitative agreement of the variation for the three bases.

Table 1

Exponents used for bases I, II, III

Basis	S _F	P _F	S _H	P _H
I	.35, 1.1, 11, 35, 110, 350, 1100, 3500	.27, .92, 3.2, 11.0, 38.0	.1483, .6577, 4.2392	1.0
II	.72, 3.6, 18, 90, 450	.48, 2.4, 12.0	"	--
III	1.25, 10.0, 80.0	.64, 3.84	"	--

Table 2

Total and orbital energies and dipole moments

Basis	Clementi	Ransil	I	II	III
Internuclear distance	1.7328	1.7328	1.75	1.75	1.75
Total energy	-100.05754	-99.53614	-100.01785	-99.40371	-95.34717
1 σ	-26.30617	-26.26612	-26.2749	-26.1094	-24.8935
2 σ	-1.61068	-1.48860	-1.5934	-1.5427	-1.3234
3 σ	-0.77459	-0.60558	-0.7502	-0.7012	-0.5901
1 π	-0.65786	-0.46863	-0.6365	-0.5963	-0.4751
4 σ	--	0.66916	0.1835	0.2567	0.4201
2 π	--	--	0.9433	2.2879	3.8714
Dipole moment	0.78	0.57	0.9239	0.8836	0.6200

Table 2 (continued)

Basis	I	II	III	I	II	III
Inter-nuclear distance	1.65	1.65	1.65	1.85	1.85	1.85
Total energy	-100.01512	-99.39937	-95.36483	-100.01404	-99.40163	-95.32455
1 σ	-26.2739	-26.1201	-24.9112	-26.2748	-26.1076	-24.8835
2 σ	-1.6150	-1.5686	-1.3645	-1.5750	-1.5227	-1.2896
3 σ	-0.7707	-0.7233	-0.6083	-0.7298	-0.6821	-0.5742
1 π	-0.6418	-0.6053	-0.4858	-0.6314	-0.5907	-0.4680
4 σ	0.1966	0.2723	0.4305	0.1690	0.2391	0.4041
2 π	0.9409	2.2804	3.8598	0.9457	2.2922	3.8785
Dipole moment	0.8937	0.8672	0.6333	0.9544	0.8990	0.6033

GAUSSIAN ORBITAL EXPONENTS

M. C. Harrison
I. G. Csizmadia

The results of a systematic method for choosing orbital exponents for Gaussian functions is given below. The method is similar to that proposed by Reeves¹ and consists of the assumption that, given optimum exponents for one free atom, optimum exponents for another free atom can be obtained by rescaling the set by a factor which is derived from the Slater rules for exponentials. A slight difficulty arises in that for a Gaussian basis, no distinction is made between 1s and 2s functions, and so it is desirable that a single scale factor should be used for this set. The scale factors given by the Slater rules are different for 1s and 2s, so a mean value is used. We restrict consideration to neutral atoms from carbon to neon, for which the Slater rules can be written

- (a) 1s exponent $Z - 0.3$
(b) 2s, 2p exponents $.325 (Z-1)$

Thus to scale Gaussian exponents from Z_1 to Z_2 , the factors should be

$\left(\frac{Z_2 - 0.3}{Z_1 - 0.3}\right)^2$ for 1s, and $\left(\frac{Z_2 - 1}{Z_1 - 1}\right)^2$ for 2s and 2p. Modifying these somewhat,

we propose that

- (I) the scale factor for 1s and 2s Gaussians should be

$$\frac{1}{2} \left\{ \left(\frac{Z_2 - 0.3}{Z_1 - 0.3}\right)^2 + \left(\frac{Z_2 - 1}{Z_1 - 1}\right)^2 \right\}$$

- (II) the scale factor for 2p Gaussians should be

$$\left(\frac{Z_2 - 1}{Z_1 - 1}\right)^2$$

Using these rules, and assuming the optimum values for Neon², we obtain the values given in Tables 1 and 2. Similarly, Tables 3 and 4 show the values derived from Nitrogen³. It should be noted that Table 4 contains values for a single p-function on free Nitrogen, as well as two additional entries which correspond to the modifications found to be necessary when a single p-function was used in NH₃ (with the Z-axis as axis of symmetry). The results may be useful in analogous situations in other molecules.

References

1. C. M. Reeves, J.C.P., July 1963.
2. M. C. Harrison, MIT SSMTG, QPR, July 1963.
3. C. M. Reeves and M. C. Harrison, J.C.P. July 1963.

Table 1. Exponent values for s-functions, derived from Neon

Atom	C	N	O	F	Ne
Factor	0.326975	0.460770	0.617540	0.797283	1.000000
3s	0.634	0.894	1.20	1.55	1.94
	5.00	7.05	9.45	12.5	15.3
	39.6	55.8	74.7	96.5	121.
5s	0.302	0.425	0.570	0.735	0.922
	1.53	2.16	2.89	3.73	4.68
	7.77	11.0	14.7	19.0	23.8
	39.5	55.6	74.5	96.2	121.
	200.	282.	378.	488.	613.
7s	0.154	0.217	0.291	0.376	0.471
	0.608	0.857	1.15	1.48	1.86
	2.39	3.37	4.51	5.83	7.31
	9.42	13.3	17.8	23.0	28.8
	37.3	52.5	70.4	90.9	114.
	146.	206.	276.	356.	447.
	575.	811.	1090.	1400.	1760.

Table 2. Exponent values for p-functions, derived from Neon

Atom	C	N	O	F	Ne
Factor	0.308642	0.444444	0.604938	0.790123	1.000000
2p	0.252	0.363	0.494	0.646	0.817
	1.48	2.13	2.90	3.79	4.80
3p	0.178	0.257	0.350	0.457	0.578
	0.923	1.33	1.81	2.36	2.99
	4.78	6.89	9.38	12.2	15.5
5p	0.0994	0.143	0.195	0.254	0.322
	0.346	0.498	0.678	0.885	1.12
	1.17	1.69	2.30	3.00	3.80
	4.07	5.87	7.99	10.4	13.2
	14.1	20.4	27.7	36.2	45.8

Table 3. Exponent values for s-functions, derived from Nitrogen

Atom	C	N	O	F	Ne
Factor	0.709107	1.000000	1.340948	1.731949	2.173006
3s	0.584	0.823	1.10	1.43	1.79
	4.92	6.94	9.31	12.0	15.1
	4.15	58.5	78.4	101.	127.
5s	0.311	.439	.589	.760	.954
	1.55	2.19	2.93	3.79	4.75
	7.72	10.9	14.6	18.9	23.7
	38.4	54.2	72.7	93.9	118.
	191.	270.	362.	468.	587.

Table 4. Exponent values for p-functions, derived from Nitrogen (both free and in NH_3)

Atom	C	N	O	F	Ne
Factor	0.694444	1.000000	1.361111	1.777778	2.250000
1p(free)	0.382	0.550	0.749	0.978	1.24
1p(x, y)	0.694	1.00	1.36	1.78	2.25
1p(z)	0.361	0.520	0.708	0.924	1.17

MAGNETIC DIPOLE-DIPOLE INTEGRALS OVER GAUSSIAN FUNCTIONS

M. C. Harrison

The two-electron integrals of the form

$$\iint \phi_A(\vec{r}_1) \phi_B(\vec{r}_1) \frac{x_{12}^2 - y_{12}^2}{r_{12}^5} \phi_C(\vec{r}_2) \phi_D(\vec{r}_2) d\tau_1 d\tau_2$$

where ϕ_A is a Gaussian centered on A, can be evaluated as follows. Consider first the integral involving just s-type Gaussians:

$$I = \iint e^{-\alpha r_{1A}^2} e^{-\beta r_{1B}^2} \frac{x_{12}^2 - y_{12}^2}{r_{12}^5} e^{-\gamma r_{2C}^2} e^{-\delta r_{2D}^2} d\tau_1 d\tau_2$$

This may be written

$$I = e^{-\frac{\alpha\beta}{\alpha+\beta} AB^2 - \frac{\gamma\delta}{\gamma+\delta} CD^2} \iint e^{-\lambda r_{1E}^2} \frac{x_{12}^2 - y_{12}^2}{r_{12}^5} e^{-\mu r_{2F}^2} d\tau_1 d\tau_2$$

where $\lambda = \alpha + \beta$, $\mu = \gamma + \delta$, $\vec{E} = \frac{\alpha\vec{A} + \beta\vec{B}}{\alpha + \beta}$, $\vec{F} = \frac{\gamma\vec{C} + \delta\vec{D}}{\gamma + \delta}$

Then since

$$\frac{x_{12}^2 - y_{12}^2}{r_{12}^5} = \frac{1}{3} \left(\frac{d^2}{dx_{12}^2} - \frac{d^2}{dy_{12}^2} \right) \left(\frac{1}{r_{12}} \right)$$

and

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{\pi}} \int_0^{\infty} t^{-\frac{1}{2}} e^{-tr_{12}^2} dt \quad r \neq 0$$

and writing

$$K = e^{-\frac{a\beta}{a+\beta} AB^2 - \frac{\gamma\delta}{\gamma+\delta} CD^2}$$

we may write

$$\begin{aligned} I &= \frac{K}{3\sqrt{\pi}} \iiint e^{-\lambda r_{1E}^2} \left(\frac{d^2}{dx_{12}^2} - \frac{d^2}{dy_{12}^2} \right) \left(t^{-\frac{1}{2}} e^{-tr_{12}^2} \right) e^{-\mu r_{2F}^2} d\tau_1 d\tau_2 dt \\ &= \frac{K}{3\sqrt{\pi}} \iiint \left(\frac{d^2}{dx_2^2} - \frac{d^2}{dy_2^2} \right) \left(e^{-\lambda r_{1E}^2} t^{-\frac{1}{2}} e^{-tr_{12}^2} \right) e^{-\mu r_{2F}^2} d\tau_1 d\tau_2 dt \\ &= \frac{K}{3\sqrt{\pi}} \iint \left(\frac{d^2}{dx_2^2} - \frac{d^2}{dy_2^2} \right) \left(e^{-\frac{\lambda t}{\lambda+t} r_{2E}^2} \frac{1}{2} \left(\frac{\pi}{\lambda+t} \right)^{\frac{3}{2}} t^{-\frac{1}{2}} e^{-\mu r_{2F}^2} \right) d\tau_2 dt \\ &= \frac{K}{6\sqrt{\pi}} \iint \left(\frac{\pi}{\lambda+t} \right)^{\frac{3}{2}} t^{-\frac{1}{2}} \left(\frac{d^2}{dx_E^2} - \frac{d^2}{dy_E^2} \right) \left(e^{-\frac{\lambda t}{\lambda+t} r_{2E}^2} e^{-\mu r_{2F}^2} \right) d\tau_2 dt \\ &= \frac{K}{6\sqrt{\pi}} \int \left(\frac{\pi}{\lambda+t} \right)^{\frac{3}{2}} t^{-\frac{1}{2}} \left(\frac{d^2}{dx_E^2} - \frac{d^2}{dy_E^2} \right) \left\{ e^{-\frac{\lambda\mu t}{\lambda\mu+\lambda t+\mu t} EF^2} \frac{1}{2} \left(\frac{\pi(\lambda+t)}{\lambda\mu+\lambda t+\mu t} \right)^{\frac{3}{2}} \right\} dt \\ &= \frac{K}{12\sqrt{\pi}} \int \left(\frac{\pi}{\lambda+t} \right)^{\frac{3}{2}} t^{-\frac{1}{2}} \left(\frac{\lambda\mu t}{\lambda\mu+\lambda t+\mu t} \right) (x_{EF}^2 - y_{EF}^2) e^{-\frac{\lambda\mu t}{\lambda\mu+\lambda t+\mu t} EF^2} \\ &\quad \left(\frac{\pi(\lambda+t)}{\lambda\mu+\lambda t+\mu t} \right)^{\frac{3}{2}} dt \end{aligned}$$

84. MAGNETIC DIPOLE-DIPOLE INTEGRALS OVER GAUSSIAN FUNCTIONS

$$= \frac{K}{3} \sqrt{\frac{\pi^5}{\lambda^3 \mu^3}} (x_{EF}^2 - y_{EF}^2) \int_0^\infty \frac{t^{3/2}}{(1+\omega t)^{7/2}} e^{-\frac{t}{1+\omega t} EF^2} dt \quad \text{where } \omega = \frac{\lambda+\mu}{\lambda\mu}$$

Changing variables to $v = \frac{\omega t}{1+\omega t}$ gives

$$I = \frac{K}{3} \sqrt{\frac{\pi^5}{\lambda^3 \mu^3}} (x_{EF}^2 - y_{EF}^2) \omega^{-5/2} \int_0^1 2v^4 e^{-\frac{EF^2}{\omega} v^2} dv$$

$$= \frac{2K}{3} \sqrt{\frac{\pi^5 \lambda^2 \mu^2}{(\lambda+\mu)^5}} \cdot (x_{EF}^2 - y_{EF}^2) \cdot f_2\left(\frac{\lambda\mu}{\lambda+\mu} EF^2\right)$$

where

$$f_m(z) = \int_0^1 v^{2m} e^{-zv^2} dv$$

The auxiliary function $f_m(z)$ is easily evaluated, and is identical to the function which occurs in the electronic repulsion integrals, for which the basic formula is

$$2K \sqrt{\frac{\pi^5}{\lambda^2 \mu^2 (\lambda+\mu)}} f_0\left(\frac{\lambda\mu}{\lambda+\mu} EF^2\right)$$

As shown by Boys (1950), basic formulae for s-type integrals may be differentiated with respect to $A_x, A_y, A_z, B_x, \dots$ etc., to yield formulae for Gaussians multiplied by powers of $x_{1A}, y_{1A}, z_{1A}, x_{1B}, \dots$ etc. Note that $\frac{d}{dz}(f_m(z)) = -f_{m+1}(z)$.

Reference

Boys, S. F., Proc. Roy. Soc., A200, 542, 1950.

MOLECULAR INTEGRALS OVER SLATER ORBITALS

D. E. Ellis

In the last report a computer program for the computation of one and two center integrals over a basis set of Slater orbitals was described¹. Storage of auxiliary functions and the use of mixed analytic and numerical integrations made increased speed and accuracy possible. Testing has been completed for all combinations of s, p, and d orbitals. Separate versions of the package are being prepared for use of real and complex orbitals.

A set of routines has been written for the three center integrals $\langle AB | \frac{1}{r_C} \rangle$, $\langle AA | BC \rangle$, and $\langle AB | AC \rangle$, being the one electron resonance, and the two electron coulomb and exchange integrals respectively. Final testing is being carried out for combinations of s, p, and d orbitals. Extension to higher orbitals will require modification of the function storage scheme, at least for the exchange integrals. Programs are being written to rotate the three center integrals into a convenient co-ordinate system.

Reference

1. D. E. Ellis, SSMTG QPR, No. 48, April 15, 1963.

THE π ELECTRONIC STRUCTURE OF THE BENZENE MOLECULE

J. W. Moskowitz
M. P. Barnett

1. Introduction

An understanding of the electronic structure of the benzene molecule is of central importance to much of theoretical organic chemistry. For this reason, and because certain formal simplifications follow from the molecule's symmetry, numerous theoretical calculations have been made of the electronic structure of benzene.^{(1) - (7)} All of these have involved simplifying assumptions and approximations that seemed reasonable, but recent developments in high speed computing make it possible to treat the problem in ways that would have been prohibitively difficult in the past. This paper presents some results that were obtained using (i) accurate values for the three and four-centre integrals which hitherto have been ignored or approximated, and (ii) rather more configurations than have been used by earlier workers. The calculations can be compared most directly with those of Parr, Craig and Ross⁽⁶⁾ (PCR) which they extend in the two ways just mentioned. Past theoretical work on the benzene molecule is reviewed briefly in Section II, and the results of the new calculations are presented and discussed in Section III.

2. Previous calculations

The benzene molecule was first treated by Goeppert-Mayer and Sklar⁽¹⁾ (GMS) as a system of six interacting $2p\pi$ electrons in the electrostatic field of the molecular core. Lykos and Parr⁽²⁾, and McWeeny⁽³⁾ have discussed the separability of the sigma and pi electrons in benzene. They conclude that an operator H_π that is quantum mechanically meaning-

ful, can be defined for the π electrons if the sigma electrons occupy a fully symmetric closed shell configuration. The expectation value of the operator H_π then gives the π electron contribution to the total energy including sigma- π coulomb and exchange interactions. The Goeppert-Mayer and Sklar core approximation has been used in most of the calculations of the benzene molecule. The electrostatic potential due to this core is derived from the three further assumptions: (i) the contributions to the core potential that are due to the hydrogen nuclei and the electronic distributions surrounding them can be neglected; (ii) the contribution to the potential that is due to the carbon nuclei and their electronic distribution can be approximated as the potential due to carbon atoms in their valence states minus the charge distribution of an electron in a π orbital; (iii) all exchange terms with the core electrons can be neglected.

The molecular orbitals (MO's) for the six π electrons can be written in the form of Bloch sums or symmetry orbitals

$$b_m = N_m^{-\frac{1}{2}} \sum_j e^{i\pi m j / 3} x_j(\phi - \pi j / 3) \quad (1)$$

where $x_j(\phi - \phi_j)$ is an atomic orbital at the site ϕ_j . For $m = 0, 3$ the orbitals are non-degenerate and for $m = \pm 1, \pm 2$ they are doubly degenerate. The benzene molecule belongs to the point group D_{6h} . The orbitals may be conveniently designated a_{2u} , b_{1g} , e_{1g} , and e_{2u} respectively. Due to the high symmetry of the hexagon, the MO's are completely determined in the LCAO approximation.

In the ground state a_{2u} and e_{1g} are fully occupied. Goeppert-Mayer and Sklar examined the excited states which differ in configuration from the ground state by having one electron excited to the e_{2u} state, leaving a hole in the e_{1g} state. The symmetries of these excited states are ${}^1, {}^3B_{1u}$, ${}^1, {}^3B_{2u}$, and ${}^1, {}^3E_{1u}$ respectively. In calculating the energies all three and four-center molecular integrals were neglected by Goeppert-Mayer and Sklar. The agreement with the observed positions of the singlet levels was fairly good. The calculated values of the triplet levels, however, were much too low.

Roothaan and Parr⁽⁴⁾ extended these calculations by including estimates for all of the multicenter molecular integrals. The result was a considerable upward shift of the excited levels. The calculated energies of the excited singlet levels all tend to be considerably higher than the observed energies of these states. Niira⁽⁵⁾ has elaborated on the calculation by taking account of the interaction of the sigma and π electrons. He used a set of symmetry orbitals for the sigma electrons constructed from sp^2 -hybrid orbitals on

88. THE π ELECTRONIC STRUCTURE OF THE BENZENE MOLECULE

the carbon atoms and the $1s$ orbitals of the hydrogens. Niira found an increase in the energies of all the excited states relative to the ground state. The inclusion of this sigma- π interaction therefore puts all the singlet-singlet transitions much further into the ultraviolet than is observed experimentally.

The introduction of limited configuration interaction (CI) into the calculation is due to Parr, Craig, and Ross.⁽⁶⁾ These workers include states which differ in configuration by the excitation of either one or two electrons from the orbitals that are occupied in the ground state. Extensive movements of the levels result when the configuration interaction is included. Shifts even occur in the relative positions of some of the levels.

The benzene molecule has been studied extensively in the alternant molecular orbital approximation (AMO) by Lowdin, Pauncz, and de Heer.⁽⁷⁾ By forming suitable linear combinations of bonding and antibonding MO's it is possible to construct basis orbitals which are semi-localized on alternant atomic sites so that electrons with different spin are kept apart spatially. The energy stabilization which they found for all the states which they considered, using this AMO method, with two variable parameters, was more than 90 per cent of the energy stabilization which we obtain with the CI treatment that is reported below.

3. Present calculations

A study of the excited energy levels of the benzene molecule using the core approximation has been completed recently by the authors. This employs a larger configuration interaction than has been used previously for benzene, as well as an accurate computation of all multicenter integrals. The formal treatment of the π electron system is identical with that for a hexagonal ring of hydrogen atoms.⁽⁸⁾ When all possible configurations arising from the six π electrons are included, the number of possible determinantal functions is 924. The 37 orbital configurations $0^2 1^4$, $0^2 1^3 2$, \dots , $2^4 3^2$ give rise to 268 possible multiplets. Maximum use of spin and space symmetry allows a considerable reduction in the size of the secular equation. The one electron energies in the Goeppert-Mayer and Sklar approximation are of the form:

$$N_m(E_m - W_{2p}) = H_{11} + 2H_{12} \cos(\pi m/3) + 2H_{13} \cos(2\pi m/3) + H_{14}(\cos \pi m) \quad (2)$$

where

$$H_{pq} = - \sum_{\substack{r=1 \\ r \neq q}}^6 [(r/pq) + (pq/rr)] \quad (3)$$

$$(r/pq) = - \int U_r(1) \chi_p^*(1) \chi_q(1) d\tau \quad (4)$$

$$(pq/rs) = \int \chi_p^*(1) \chi_q(1) \frac{1}{r_{12}} \chi_r^*(2) \chi_s(2) d\tau_{12} \quad (5)$$

and N_m is a normalizing factor, W_{2p} is the energy of a $2p\pi$ -electron of a carbon atom in its valence state, and $U_r(1)$ is the potential energy of a neutral, spherically symmetric, r^{th} carbon atom.

The results of the configuration interaction calculation are displayed in Table I. The first two columns repeat the calculation of Parr, Craig, and Ross in which one electron energies were obtained according to the GMS core approximation, two center electron repulsion integrals were computed accurately, and three and four-center integrals were approximated by the method of London and Sklar. The agreement with the original hand calculation is good except for the CI calculation on the ${}^3B_{1u}$ state for which PCR report a value of 4.1 ev. The third column contains the result of a complete CI calculation within the π basis using the PCR integrals.

The calculation is repeated in columns four and five using accurate values for the electronic interaction integrals. The multicenter one and two electron integrals were computed by means of the zeta function expansion method developed by Barnett and Coulson.^{(9), (10)} The values were checked against the recently reported results of Karplus and Shavitt.⁽¹¹⁾

The inadequacy of the W_{2p} approximation has been discussed by Stewart⁽¹²⁾ and by others. The choice of an adequate core approximation has been investigated in considerable detail by Ruedenberg.⁽¹³⁾ The one electron Hamiltonian is split into two parts: (i) a part that accommodates the nuclear framework and the kinetic energy. This part can be regarded as "a short range force". (ii) a coulombic part that is due to the charge cloud of the π electrons of the delocalized system. This part can be regarded as a "long range force". The matrix elements of the short range forces decrease so rapidly with distance that only the nearest neighbor interactions are retained in Ruedenberg's treatment. This amounts to the use of a "tight binding" approximation. All the matrix elements of long range forces are computed by Ruedenberg who also allows the orbital exponent ζ of the atomic orbital χ_p to differ from the orbital exponent ζ_c of the four orbitals that form the core which produces the electrostatic potential $U_r(1)$ of Eq. (4). The values of ζ and ζ_c are chosen by reference to the known values for the ionization potential and the electron affinity of the valence state of carbon. Columns six and seven of our Table I show the result of a recalculation based on the "tight binding" approximation, using accurate values for the multicentre integrals. The values used for ζ and ζ_c are 1.6178932 and 1.12863045 respectively.

90. THE π ELECTRONIC STRUCTURE OF THE BENZENE MOLECULE

We have performed a second order perturbation theory treatment as well as a one parameter, alternant molecular orbital calculation on the ground state. The results are displayed in Table II. Since the MO's are solutions of a Hartree-Fock Hamiltonian, Brillouin's theorem applies, and the only matrix components which exist are those connecting the ground state with doubly substituted configurations. There are eight such configurations which interact with the ground state and in the CI treatment their coefficients are large, as anticipated. The 9×9 secular equation between these states has been diagonalized. To help visualize the complex wave function the first order density matrix in the MO basis is given in Table III. Due to the high symmetry the MO's also are the natural spin orbitals, and the first order density matrix is diagonal.

Several points arise from an analysis of the tabulated results. The most striking is the fact that improving the configuration interaction tends to decrease the multiplet separation. This is particularly true for the important ${}^3B_{1u}$ state. In general, the more that the π wave function is improved through CI, the worse is the agreement with experiment. This seems to be true regardless of the core approximation that is chosen. Moreover, there is no a priori method for choosing the important configurations. The use of accurate values for the exact integrals does not have any substantial effect on the energy level scheme. The wave functions, however, are quite sensitive to the use of accurate integrals as is shown by the change in both the eigenvectors and the first order density matrices.

The above results lead one to conclude with de Heer¹⁴ that irrespective of the problem of electron correlation, "there is an essential defect in our present quantitative approach to the quantum chemistry of conjugated hydrocarbons." A possible remedy would be to explicitly include the sigma electrons. A recent extended Hückel calculation by Hoffman⁽¹⁵⁾ would seem to lend support to this point of view. Hoffman found that the lowest bonding π orbital of benzene was located below some of the sigma levels.⁽¹⁶⁾ This implies that sigma- π interaction may be of greater importance than heretofore considered. Despite the great complexity of the problem work in this direction is in progress.

Table I

Electronic Energy Levels of Benzene (ev.) calculated by: (a) PCR Integrals GMS Core, Single Configuration, (b) and (c) PCR Integrals with N Interacting Configurations, (d) GMS Core Accurate Integrals, (e) GMS Core Accurate Integrals with CI, (f) Ruedenberg Core Accurate Integrals, (g) Ruedenberg Core with CI, (h) Observed.¹

State	a MO	b CI(N)	c CI(N)	d MO	e CI(N)	f MO	g CI(N)	h obsd.
$1A_{1g}$	0.0	0.0(9)	0.0(22)	0.0	0.0(22)	0.0	0.0(22)	0.0
$3B_{1u}$	3.09	3.65(5)	2.51(18)	3.07	2.56(18)	3.99	3.07(18)	3.66
$3B_{2u}$	5.75	8.24(4)	8.17(15)	5.56	7.95(15)	5.76	7.64(15)	5.76
$3E_{1u}$	4.42	4.55(12)	3.81(33)	4.32	3.82(33)	4.87	3.65(33)	4.69
$1E_{1u}$	9.77	9.79(11)	9.74(27)	9.76	9.69(27)	10.4	10.0(27)	6.75
$1B_{2u}$	5.88	4.16(5)	3.09(13)	5.80	3.58(13)	8.39	4.10(13)	4.89
$1B_{1u}$	7.25	8.89(6)	8.92(16)	7.10	8.77(16)	8.16	8.85(16)	6.14
$5A_{1g}$	6.11	5.90(4)	6.27(4)	5.94	6.30(4)	5.21	5.44(4)	-----
$7B_{1u}$	8.52	11.24(1)	11.61(1)	-----	-----	-----	-----	-----

1. D. R. Kearns, J. Chem. Phys., **36**, 1608 (1962).

92. THE π ELECTRONIC STRUCTURE OF THE BENZENE MOLECULE

Table II

Electronic Energy of the Ground State ($^1A_{1g}$) in Atomic Units (2 Ryd) by:
 (a) GMS Core PCR Integrals, (b) GMS Core Accurate Integrals,
 (c) Ruedenberg Core Accurate Integrals.

	a	b	c
MO	-4.2421	-4.2505	-9.0534
CI(9)	-4.3420	-4.3508	-9.1471
CI(22)	-4.3557	-4.3644	-9.1596
2nd Order	-4.3283	-4.3398	-9.1369
AMO	-4.3303	-4.3379	-9.1260
λ	0.69	0.70	0.72

Table III

First order Density Matrix for the Ground State ($^1A_{1g}$) in MO Basis with
 CI by: (a) PCR Integrals GMS Core, (b) GMS Core Accurate Integrals,
 (c) Ruedenberg Core Accurate Integrals.

CI(N)\ ^m	0	± 1	± 2	3
a (22)	1.9162	1.8034	0.1970	0.0830
b (22)	1.9172	1.8086	0.1932	0.0793
c (22)	1.8922	1.8465	0.1634	0.0879
a (9)	1.9404	1.8583	0.1421	0.0587
b (9)	1.9410	1.8620	0.1392	0.0566
c (9)	1.9279	1.8936	0.1118	0.0612

References

1. M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys., 6, 645 (1938).
2. P. G. Lykos and R. G. Parr, J. Chem. Phys., 25, 1301 (1956).
3. R. McWeeny, Proc. Roy. Soc., A223, 306 (1954).
4. C. C. J. Roothaan and R. G. Parr, J. Chem. Phys., 17, 1001 (1949).
5. K. Niira, J. Phys. Soc., Japan, 8, 630 (1953).
6. R. Parr, D. P. Craig, and I. Ross, J. Chem. Phys., 18, 1561 (1950).
7. a. R. Pauncz, J. de Heer, and P. O. Lowdin, J. Chem. Phys., 36, 2247 (1962), b. R. Pauncz, J. Chem. Phys., 37, 2739 (1962), c. J. de Heer, J. Phys. Chem. 66, 2288 (1962).
8. J. W. Moskowitz, J. Chem. Phys. 37, 677 (1963).
9. M. P. Barnett and C. A. Coulson, Phil. Trans. Roy. Soc., A243, 221 (1951).
10. M. P. Barnett, Methods of Computational Physics, Vol. II, Academic Press (in press).
11. M. Karplus and I. Shavitt, J. Chem. Phys., 38, 1256 (1963).
12. E. T. Stewart, Proc. Phys. Soc., (London), 75, 220 (1960).
13. K. Ruedenberg, J. Chem. Phys., 34, 1861-1913 (1961).
14. J. de Heer, Rev. Mod. Phys., (1963) in press.
15. R. Hoffman, J. Chem. Phys., (1963), to appear.
16. This possibility was also suggested by J. C. Slater. "Quantum Theory of Molecules and Solids, Vol. 1," McGraw-Hill, N. Y., (1963).